DESULFURDIMERIZATION OF DITHIOACETALS WITH TUNGSTEN HEXACARBONYL

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A thesis submitted in partial fulfilment of the

requirements for the degree of

Master of Philosophy in

The Chinese University of Hong Kong

1989

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ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my advisor, Dr. Tien-Yau LUH, for his patient guidance, encouragement and opinion in the research work and the preparation of this thesis. His kindness and extraordinary help make the completion of this thesis become an easy job.

I am indebted to Messers. Y. H. LAW, K. W. KWONG, C. W. FUNG and S. F. LUK for carrying out nmr, mass spectral and FT-IR measurements. Thanks are also due to Department of Chemistry, National Taiwan University for elemental analyses.

This research work was made possible by the generous financial support of the Croucher Foundation.

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July, 1989.

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ABBREVIATIONS

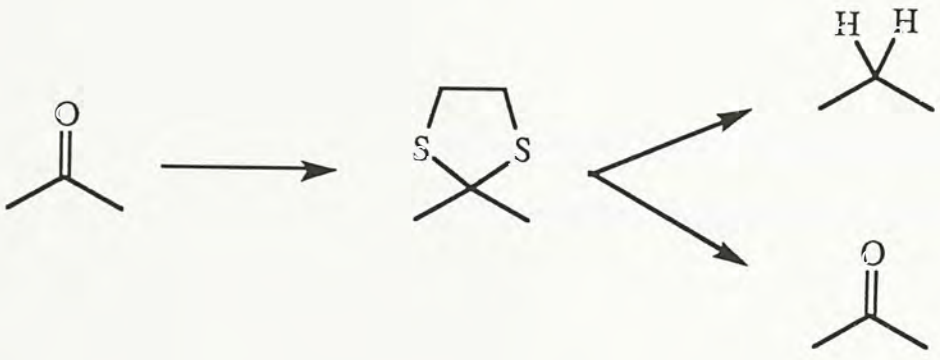
THF:	Tetrahydrofuran
TMS:	$(CH_3)_3Si$
TMSCl:	Trimethylsilylchloride
DMTSF:	dimethyl(methylthio)sulfonium fluoroborate
Tr:	Ph_3C
Np:	napthalene
dppe:	1,2-bis(diphenylphosphino)ethane
PPA:	polyphosphoric acid
NBS:	N-bromosuccinimide
AIBN:	azobisisobutyronitrile

ABSTRACT

Tungsten hexacarbonyl in refluxing chlorobenzene has been found to be an effective reagent for the desulfurdimerization of dithioacetals to give the corresponding dimeric olefins in good to excellent yields. The mechanism for this reaction has been investigated. Thioketones have been isolated from the reactions of highly crowded dithioacetals. The mechanism for the formation of thioketones has been shown to occur via a new type of radical fragmentation process of dithiolane. Thermolysis of 2,2-dimethylindan-1-yl 2-thiophenoxyethyl sulfide in the presence of t-butyl adamantane-1-peroxycarboxylate (a typical radical initiator) has been studied for comparison. Thioketones have been shown to react with tungsten hexacarbonyl giving dimeric olefins and/or undergoing carbene-like insertion reaction.

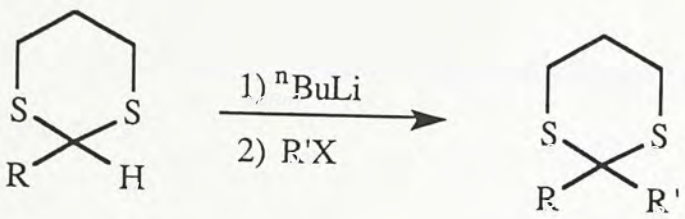
INTRODUCTION

Dithioacetal functionality was first discovered in 1885.[1] Since then, this functional group is generally served as a protective group for ketone and aldehyde, and can be removed readily by various methods.[2] Alternatively, a dithioacetal can also serve as a latent methylene moiety by hydrogenolysis to give the corresponding reduced product (eq.1). This reaction can be considered as an alternative to the Wolff-Kishner or Clemmensen reduction of a carbonyl compound. Reagents such as Raney nickel,[3] cupric chloride-zinc chloride-lithium aluminum hydride,[4] alkali metals in ammonia,[5] nickel boride[6,7] and tributyltin hydride[8] have been used for converting dithioacetals into methylene group.



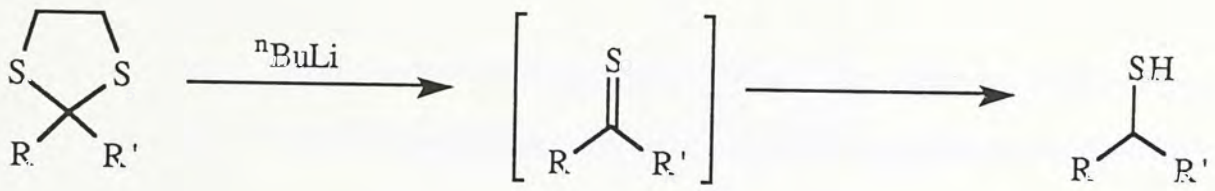
(eq.1)

Of particular importance, dithioacetal (dithiane) has been used as an umplung synthon of carbonyl equivalent (eq. 2).[9]



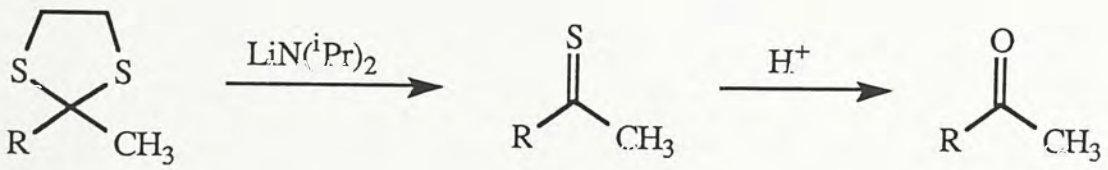
(eq. 2)

However, the synthetic applications of dithioacetal have not been explored. Treatment of dithioacetal with n-butyllithium would give thioketone which is reduced *in situ* with n-butyllithium to yield secondary mercaptan (eq.3).[10]



(eq. 3)

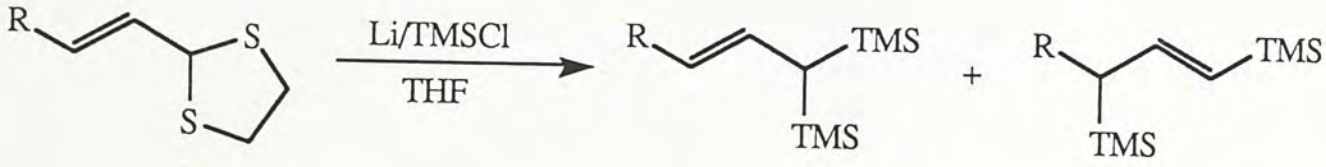
In a similar manner, lithium diisopropylamide-induced fragmentation of dithioacetal affords its corresponding thioketone which is further hydrolyzed to carbonyl compound (eq. 4).[11]



(eq. 4)

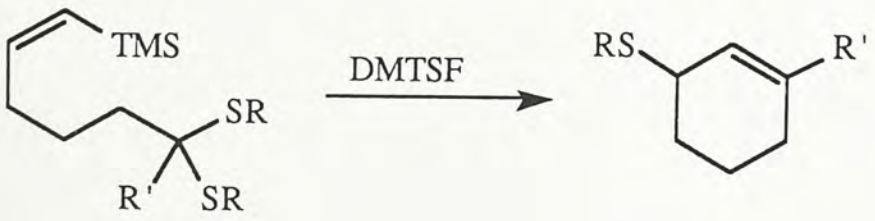
In general, dithioacetal functionality is rather stable toward nucleophilic attack. Only a few cases have been studied. For example, reductive silyation of allylic dithioacetal was

accomplished by the use of lithium metal and chlorotrimethylsilane in tetrahydrofuran (THF) (eq. 5).[12]



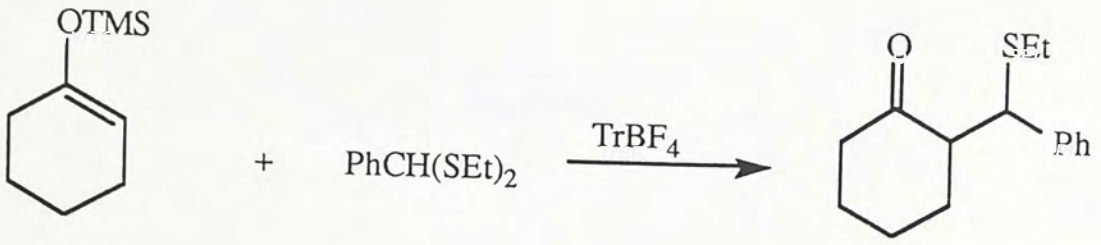
(eq. 5)

Lewis acid can facilitate the coupling process leading to the formation of the carbon-carbon bond. Trost[13] reported that dimethyl(methylthio)sulfonium fluoroborate (DMTSF) exhibits a remarkable thiophilicity for the initiation of intramolecular cyclization of vinylsilane or enol silyl ether with dithioacetal. Thus, it provides an equivalent way for a direct intramolecular aldol reaction (eq. 6).



(eq. 6)

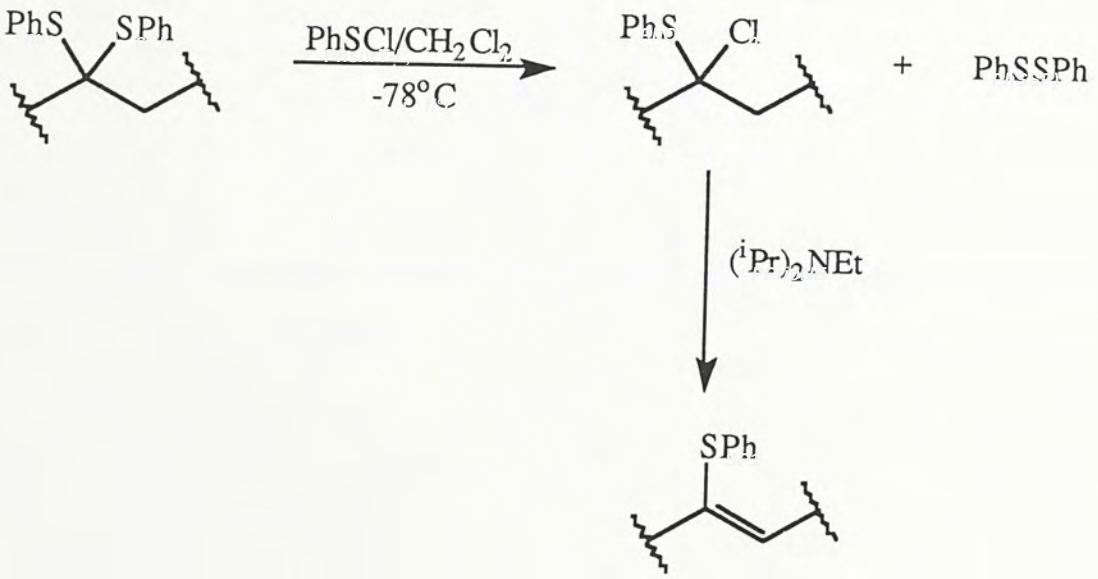
In a similar manner, trityl tetrafluoroborate also showed to be active in coupling silyl enol ether with dithioacetal (eq. 7).[14]



Tr = Ph_3C

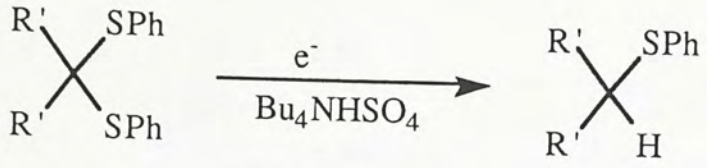
(eq. 7)

Treatment of dithioacetal with benzenesulphenyl chlorosulfide generates α-chlorosulfides which is further eliminated to vinyl sulfide (Scheme 1).[15]



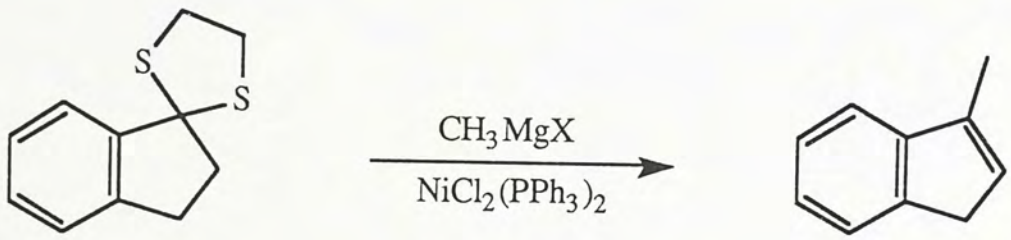
Scheme 1

One of the carbon-sulfur bond in dithioacetal could be reductively cleaved by the electrochemical method in an acidic medium to afford saturated sulfide (eq. 8).[16]



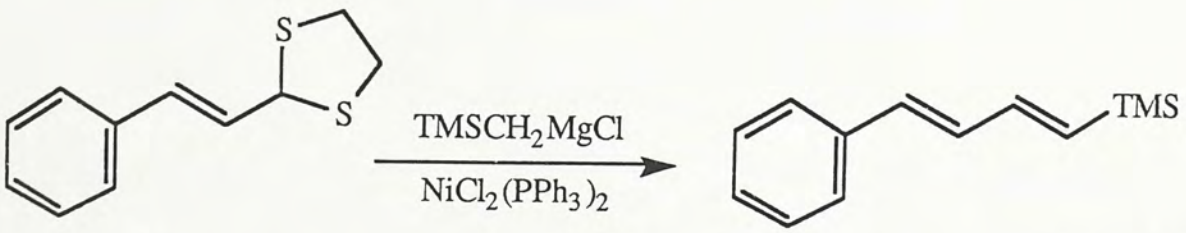
(eq. 8)

Recently, benzylic dithioacetals were found to couple with methylmagnesium iodide in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$ to give the corresponding olefins.[17]

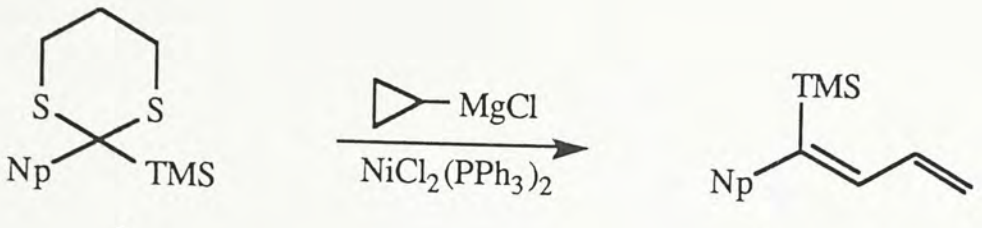


1 **2** (eq. 9)

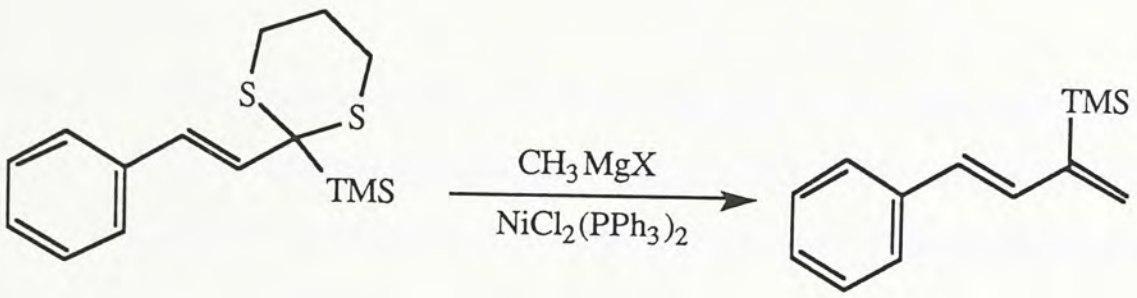
The reaction has been used in the stereoselective synthesis of substituted trimethylsilylbutadienes (eqs. 10-12).



3 **4** (eq. 10)[18]

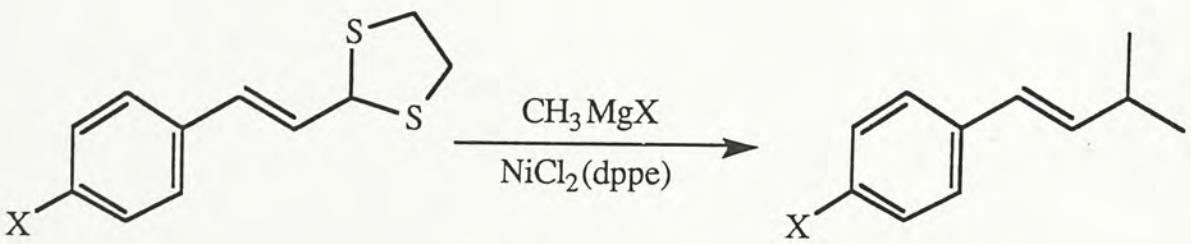


5 **6** (eq. 11)[19]



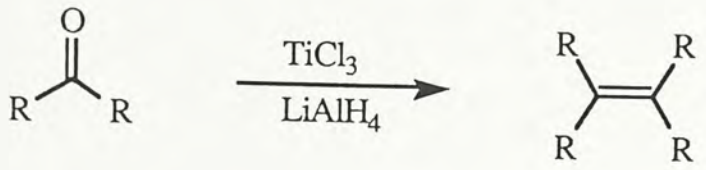
7 **8** (eq. 12)[20]

When methylmagnesium iodide is employed, the cross coupling reactions of allylic dithioacetals lead to geminal dimethylation products (eq. 13).[21]



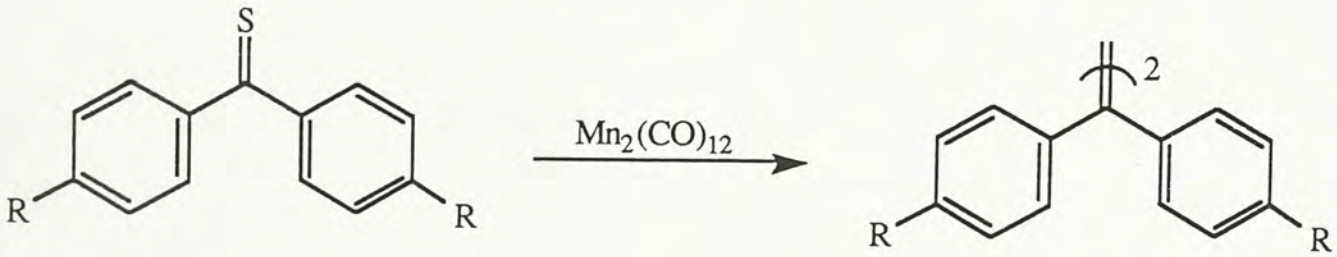
X = H, CH_3, OCH_3 (eq.13)

The reductive coupling of a carbonyl equivalent provides a versatile entry for the carbon-carbon double bond formation. Recently, McMurry and his coworkers have extensively used the low valent titanium reagent for the reductive coupling of two carbonyl moieties to afford the corresponding olefin.[22]



(eq. 14)

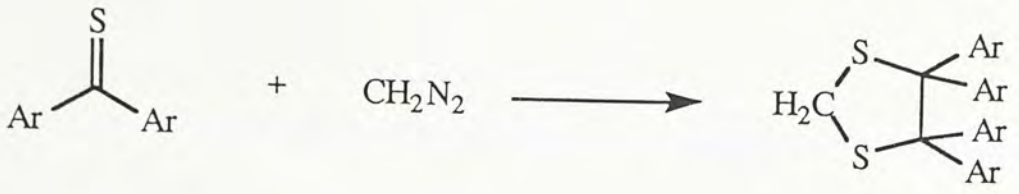
The sulfur analog has been shown to dimerize giving the dimeric product. Thus, thiobenzophenones can undergo desulfurdimerization with stoichiometric amount of dimanganese decacarbonyl in n-heptane to afford tetraaryl ethylene. Reasonable yields of olefins are also found in the reaction of the metal carbonyl with thiones having either electron-donating or withdrawing substituents (eq. 15).[23]



R= H, CH_3, CH_3O, F

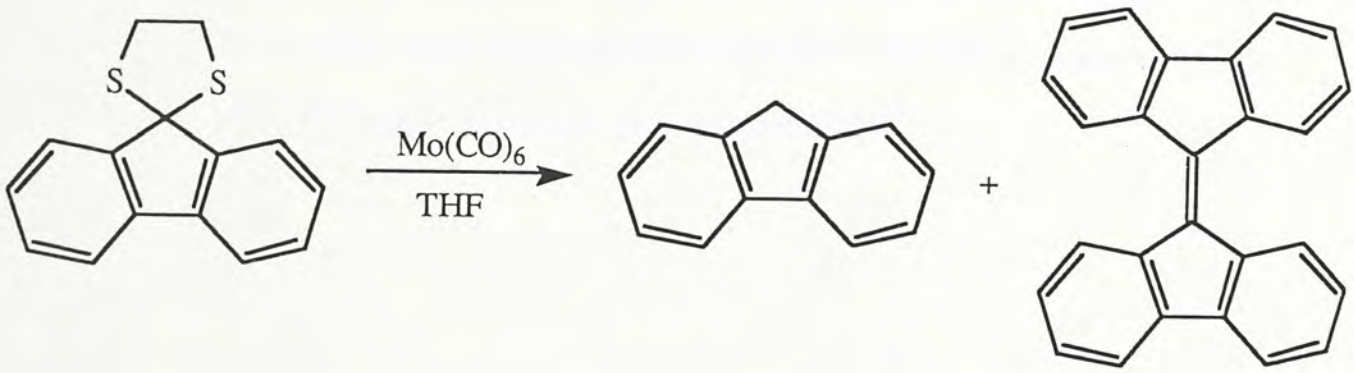
(eq. 15)

It is worthy to note that thiobenzophenone can react with the carbene precursor (eg. diazomethane) to give the corresponding dithioacetals (eq. 16)[24]



(eq. 16)

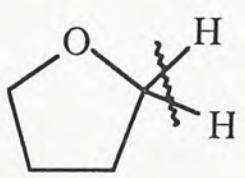
The reverse reaction while considering dithioacetal as a carbene synthon has not been explored. Molybdenum hexacarbonyl in refluxing THF has recently been reported to be a selective desulfurization reagent.[25] Reaction with 9,9-ethylenedithiofluorene **9** interestingly yields a mixture of the reduced product, fluorene **10**, and dimeric 9,9'-bifluorenylidene **11** (eq. 17).[25]



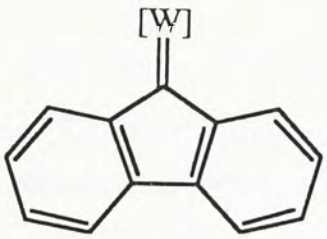
9 **10** **11**

(eq. 17)

It has been envisaged that the reduction may arise from a stepwise hydrogen abstraction from the solvent THF by some radical species generated during the course of the reaction.

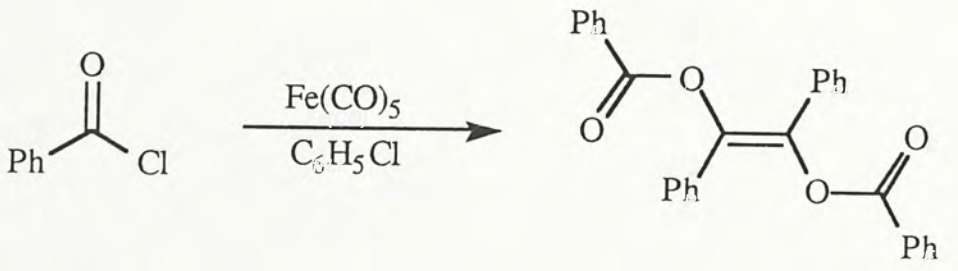


The dimeric product may be formed from the dimerization of two carbene moieties **12**.



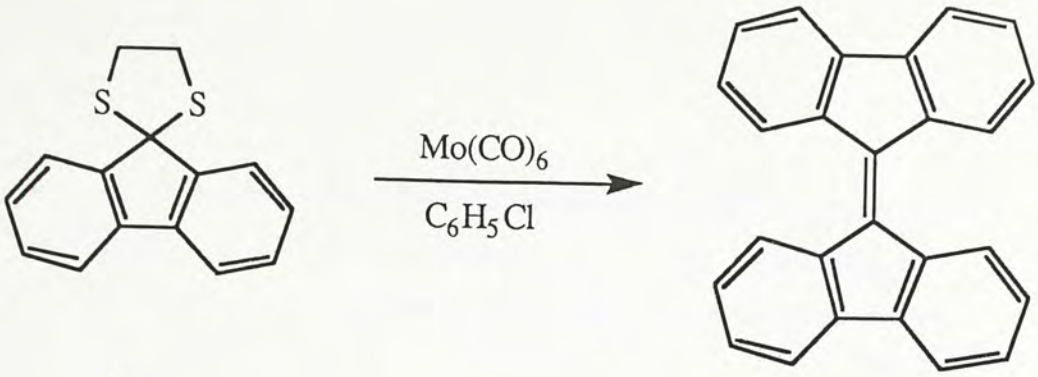
12

Chlorobenzene has been shown to be a useful solvent for the coupling of two radical intermediates in the metal carbonyl-mediated C-X bond cleavage reactions.[26,27] In this case, no hydrogen is available for radical abstraction (eq. 18).



13 **14** (eq. 18)

Indeed, when chlorobenzene was employed as the solvent for the molybdenum hexacarbonyl mediated desulfurization of 9,9-ethylenedithiofluorene,[28] the corresponding dimer was obtained exclusively (eq. 19).



9 **11** (eq. 19)

Tungsten hexacarbonyl has been shown to be more reactive in the desulfurdimerization of dithioacetals.[29] Table 1 outlines some useful examples.

Table 1: **Desulfurdimerization of dithioacetals with tungsten hexcarbonyl**

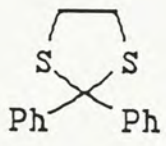
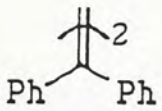
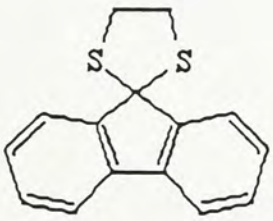
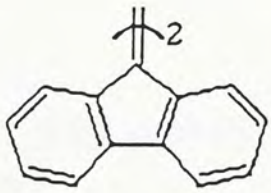
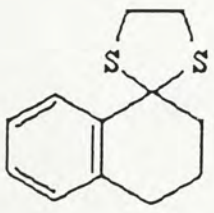
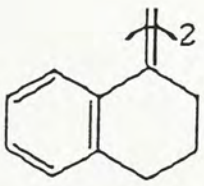
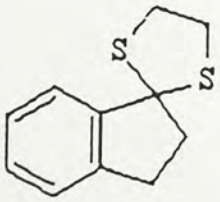
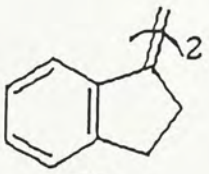
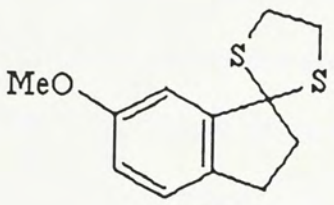
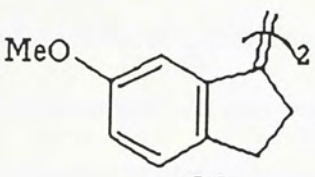
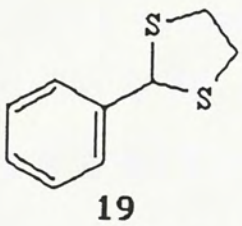
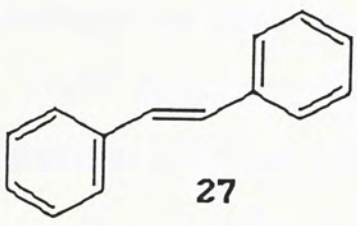
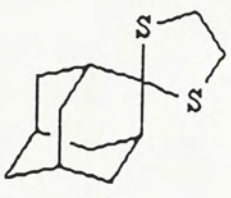
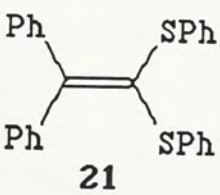
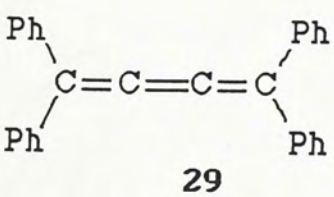
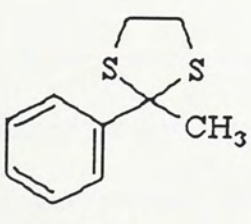
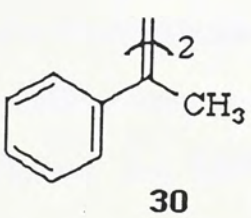
Dithioacetal	Dimer	Yield(%)
 **15**	 **23**	97
 **9**	 **11**	93
 **16**	 **24** Z-isomer	61
 **17**	 **25** Z-isomer	62

Table 1 (Cont.)

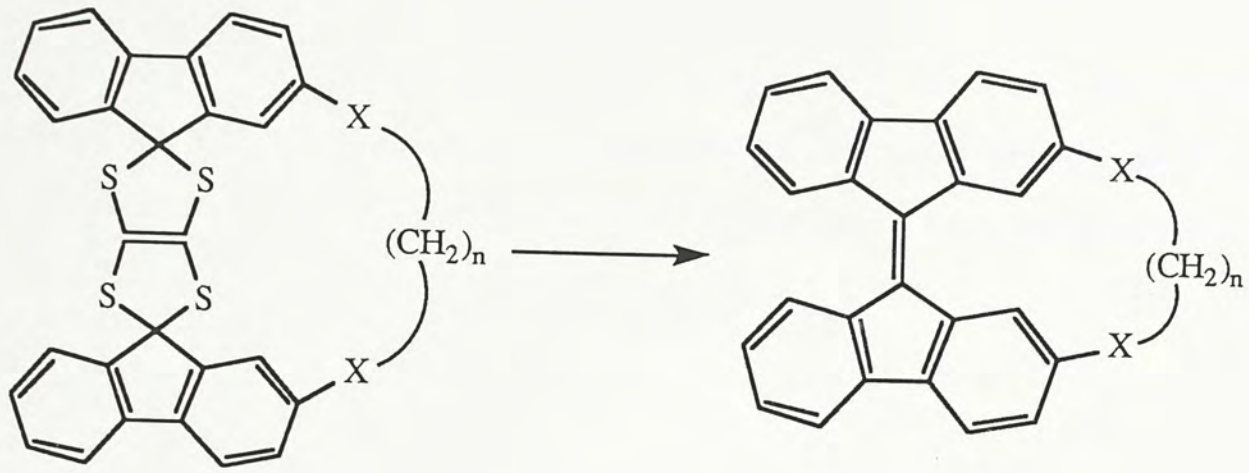
Dithioacetal	Dimer	Yield(%)
 **18**	 **26** E-isomer	55
 **19**	 **27**	45
 **20**	 **28**	71
 **21**	 **29**	75
 **22**	 **30** E : Z = 1: 1	59

Benzophenone and fluorenone dithioacetals **15** and **9** yield the respective dimers **23** and **11**. Tetralone and indanone derivatives, on the other hand, gave in slightly lower yields the dimers **23** and **26**. trans-Stilbene **27** was obtained from the reaction of the benzaldehyde derivative **19**. Adamantanone dithioacetal **20** also afforded the desired olefin **28** in good yield. Even ketene dithioacetal **21** can be converted into cumulene **29**.

The reaction shows stereoselectivity in cases with significant difference in steric environment between the olefinic isomers. When such discrepancy is lifted, the selectivity no longer holds. As a result, acetophenone dithioacetal **22** yielded a mixture of E and Z-dimethylstibenes **30**. In a similar manner, reactions of 2-substituted fluorenone dithioacetals gave E/Z isomeric mixture of bifluorenylidenes (eq. 20).

X = OMe, Br, OAc E and Z (eq. 20)

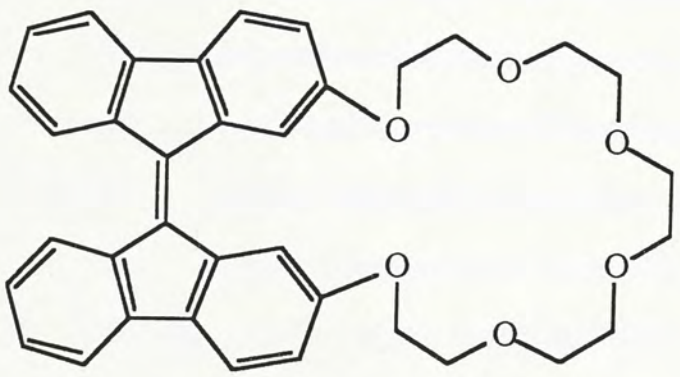
Stereospecific syntheses of substituted bifluorenylidenes, however, can be achieved by employing the bridging strategy and intramolecular desulfurdimerization reaction. Thus, (Z)-2,2'-disubstituted bifluorenylidenes (eq. 21)[30] and bifluorenylidene-hinged crown ethers **31**[31] are synthesized in good yields. The first chiral bifluorenylidene **33** was synthesized by intramolecular desulfurdimerization of two fluorenone dithioacetal moieties linked with a chiral bridge (eq. 22).[32]



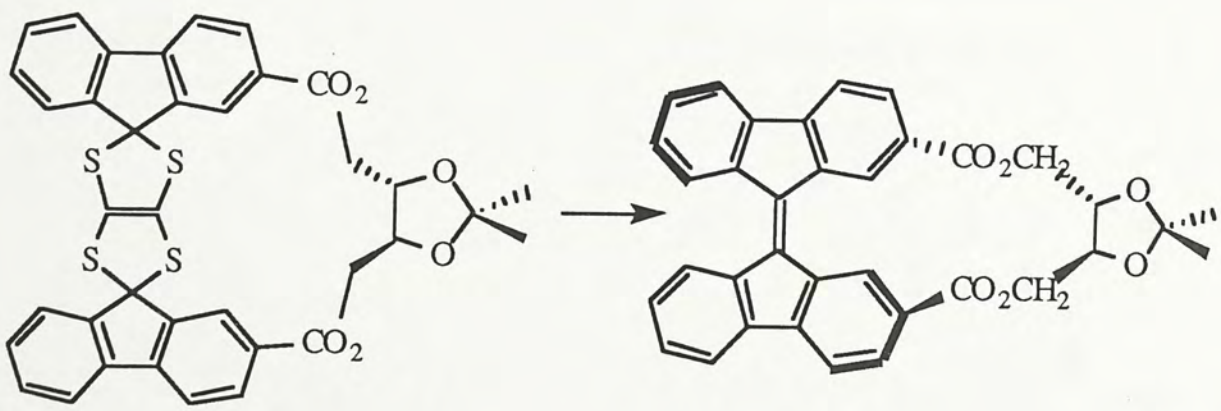
X = O, CO_2

n = 2,3,4

(eq. 21)



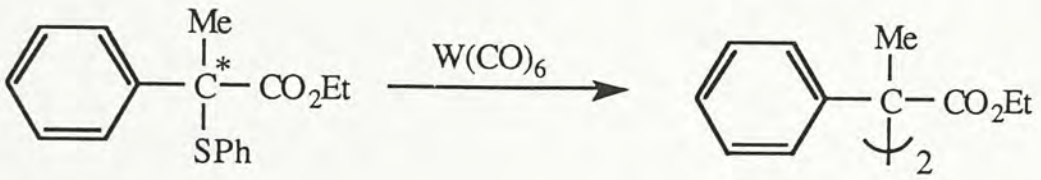
31



32 **33**

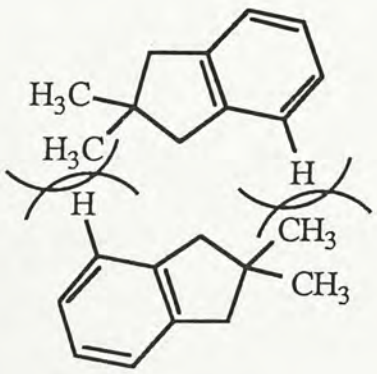
(eq.22)

Although the reaction may have synthetic value, the mechanism remains unresolved. Tungsten hexacarbonyl mediated carbon-sulfur bond cleavage reaction of mercaptans and thioethers has recently been shown to occur via a free radical mechanism (eq. 23).[33]



34 **35** (eq. 23)

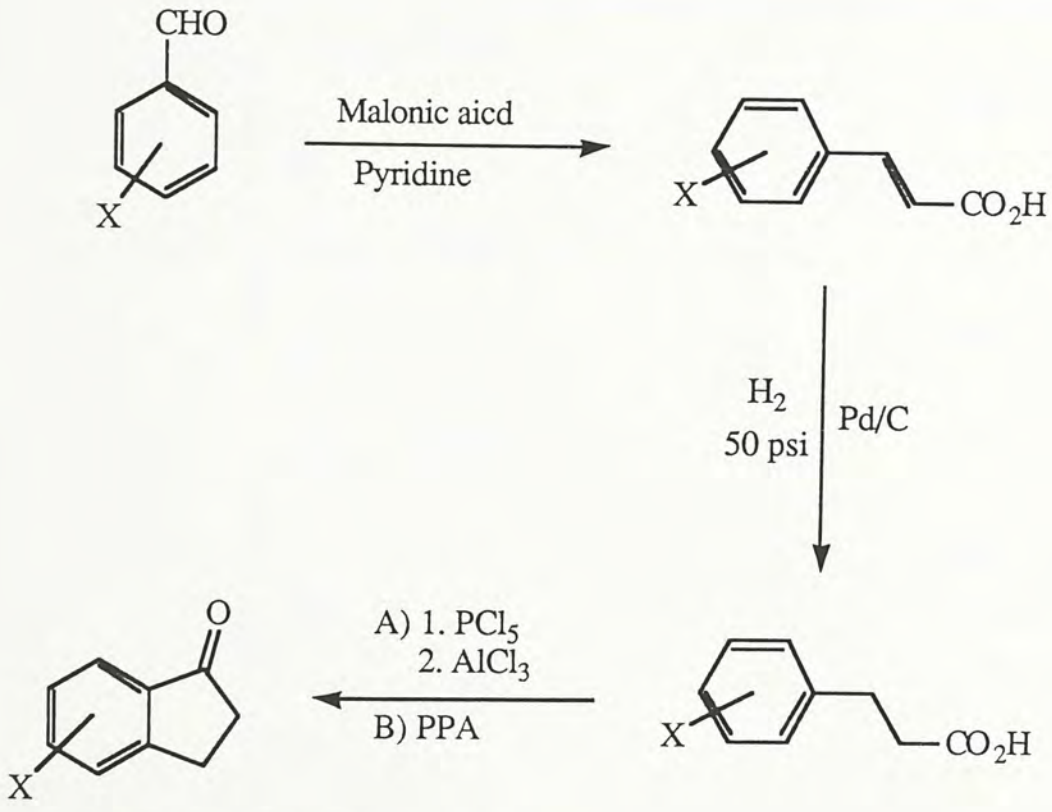
The two carbon-sulfur bonds in dithioacetal may cleave at different stage and it will be highly interesting if any intermediate compound(s) could be detected. The intrinsic idea of designing such an experiment is to treat a highly crowded dithioacetal under the reaction conditions such that intermolecular coupling step might be very slow. As seen from Table 1, indan-1-one dithioacetal derivatives gave dimers in good yield. Thus, an ideal starting point will be to introduce methyl groups at α-position to the dithioacetal. When these two carbene moieties come together, the bulkiness between the methyl groups and the peripheral H's on the aromatic ring will slow down the coupling rate. Intermediate compound(s) may be detected. In this thesis, a series of 2,2-dimethyl substituted indan-1-one dithioacetals were synthesized for the study on the mechanism of desulfurdimerization reaction.



RESULTS AND DISCUSSION

Synthesis of substituted indan-1-ones

6-Substituted indan-1-ones used in this investigation were prepared from 4-substituted benzaldehyde by modified literature procedures as outlined in Scheme 2.[34]



X = 5-Me, 6-Me, 6-OMe

Scheme 2

Condensation of substituted benzaldehydes with malonic acid in pyridine afforded substituted cinnamic acids. Hydrogenation of cinnamic acids in the presence of a catalytic amount of Pd/C (5%) gave substituted phenylpropionic acids. Ring cyclization of

substituted phenylpropionic acids could be furnished by converting to their corresponding acid chlorides with phosphorous pentachloride, followed by the reaction with aluminum chloride. Alternatively, treatment of **42** with polyphosphoric acid afforded **52**. The yields of these compounds are listed in Table 2 and 3.

Table 2: Preparation of substituted cinnamic acid and phenylpropionic acid

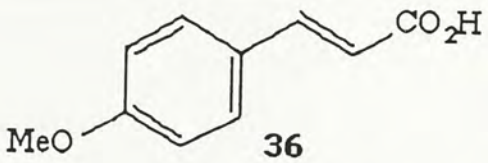
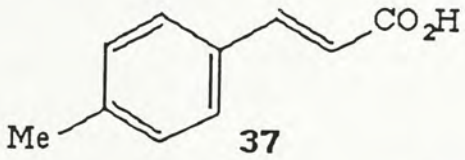
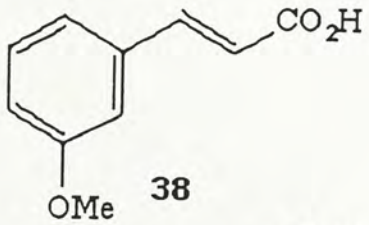
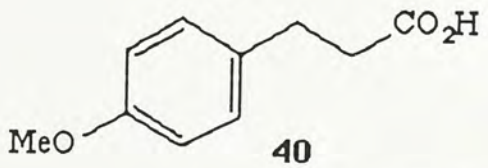
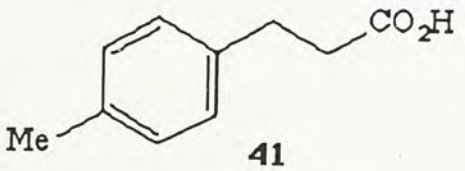
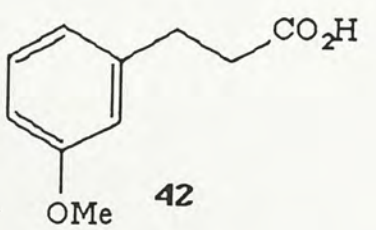
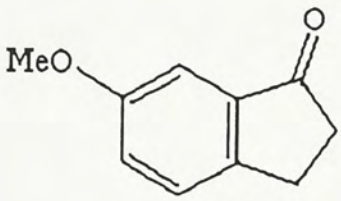
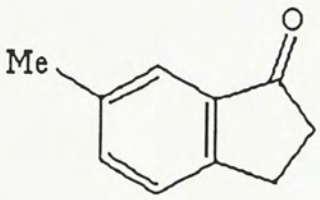
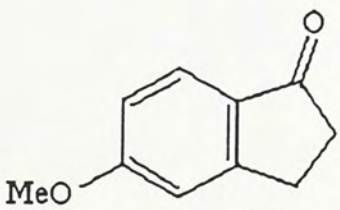
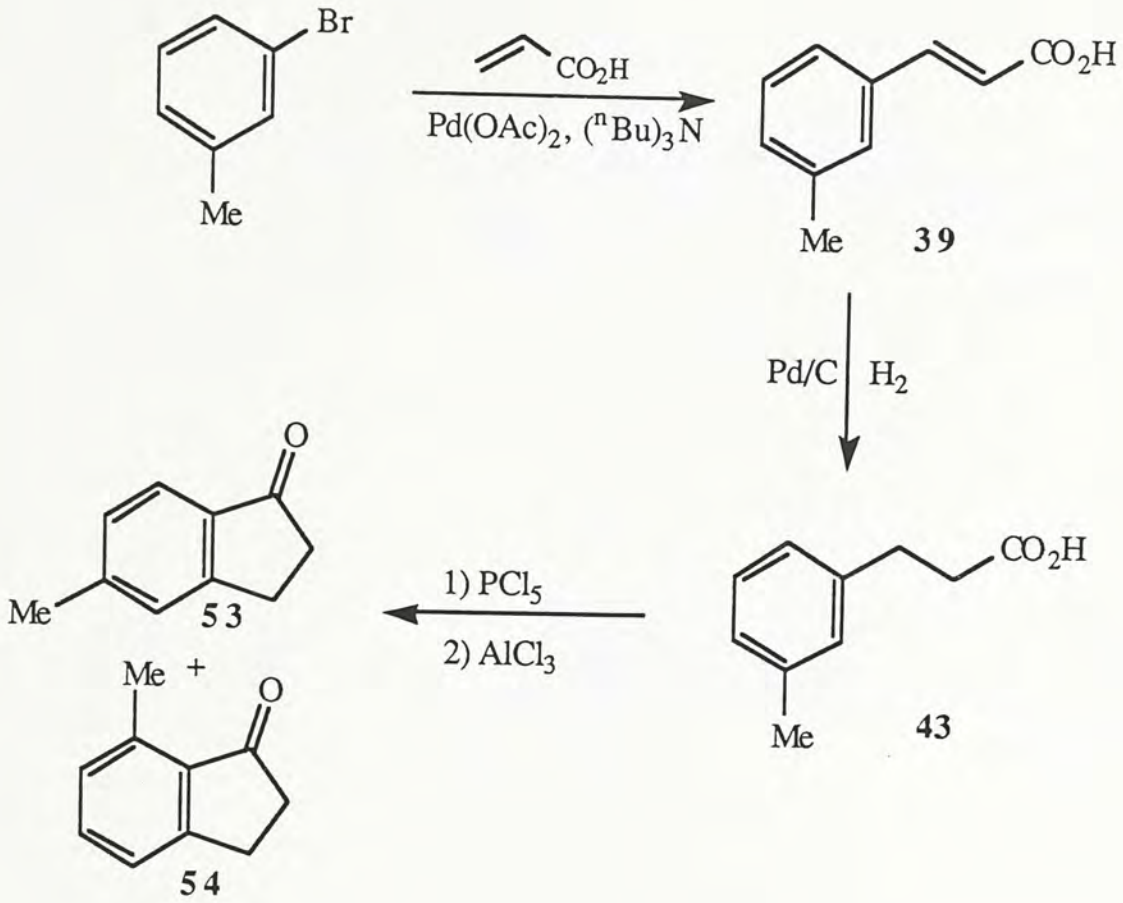
Compounds	Yield (%)
 **36**	96
 **37**	90
 **38**	84
 **40**	99
 **41**	98
 **42**	98

Table 3: Preparation of substituted indan-1-ones

Compound	Method of cyclization*	Yield (%)
 **50**	A	74
 **51**	A	64
 **52**	B	89

*Method A: 1)PCl_5 2) $AlCl_3$
Method B: PPA

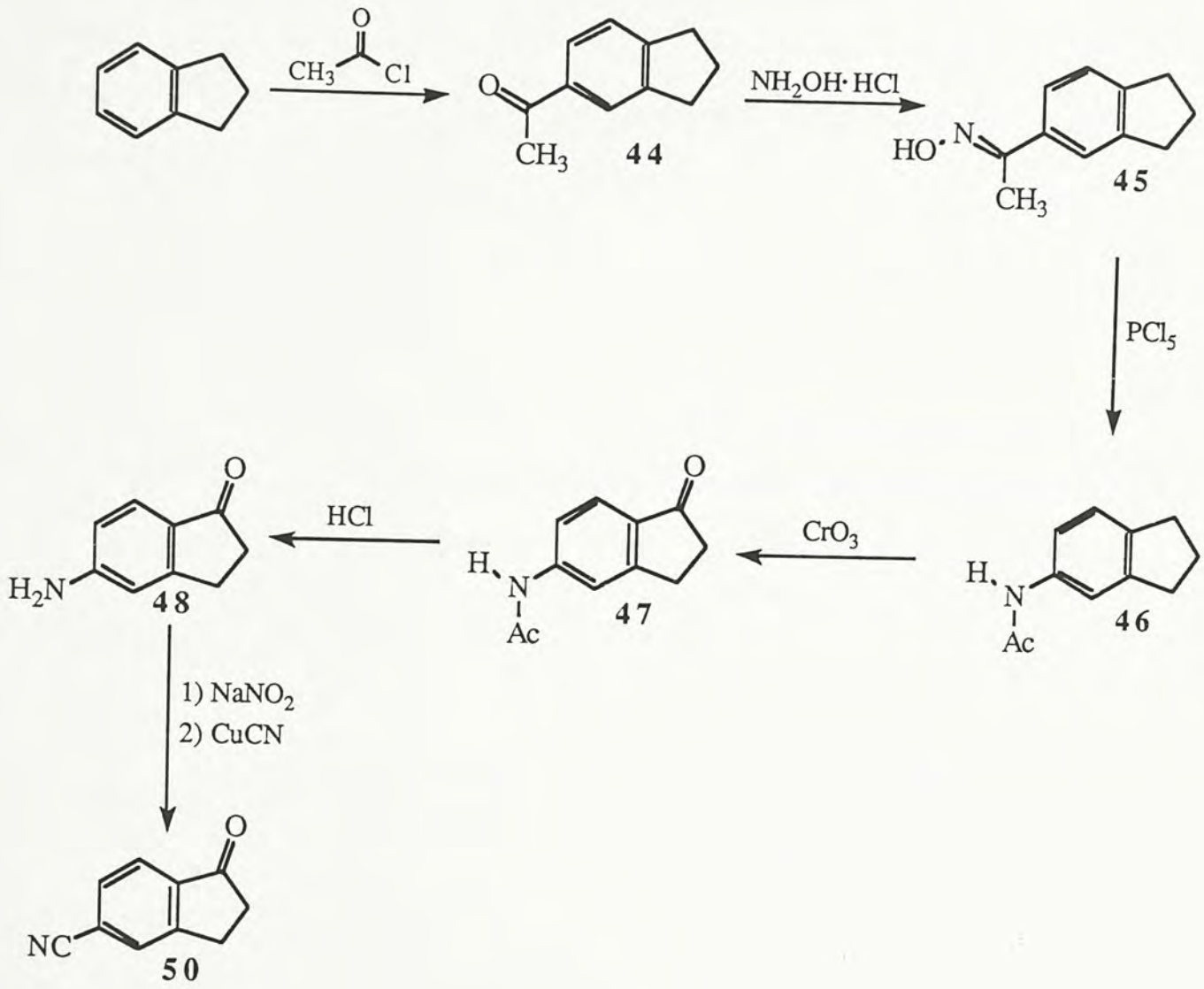
5-Methylindan-1-one **53** and 7-methylindan-1-one **54** were prepared from 3-bromotoluene by similar methods as outlined in Scheme 3.



Scheme 3

3-Bromotoluene was converted to 3-methylcinnamic acid **39** in 79% yield by coupling with acrylic acid in the presence of palladium acetate as catalyst.[35] 3-Methylcinnamic acid **39** was then hydrogenated to give 3-(3-methylphenyl)propionic acid **43** in quantitative yield. Finally, 5-methylindan-1-one **53** and 7-methylindan-1-one **54** were obtained in 47% and 45% yields, respectively from the reaction of the corresponding propionic acid and phosphorous pentachloride, then with aluminum chloride followed by chromatographic separation.

Since Friedel-Crafts ring cyclization is difficult for electron withdrawing groups, a different strategy for the synthesis of 5-cyanoindan-1-one **49** is outlined in Scheme 4.[36]



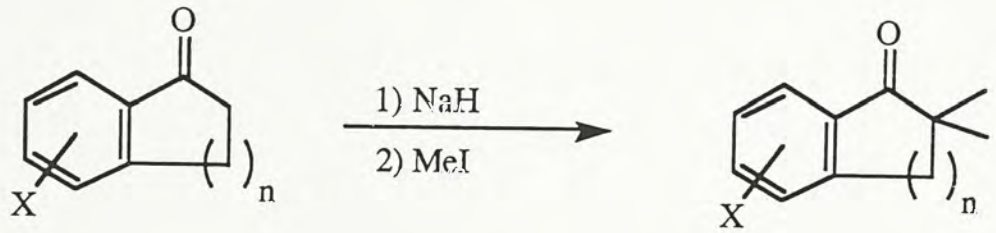
Scheme 4

Acetylation of indane in dichloromethane using aluminum chloride and acetyl chloride afforded 5-acetylindane **44** in 91% yield. Treatment of 5-acetylindane **44** with one equivalent of hydroxylamine gave its corresponding oxime **45**. Without further purification, oxime **45** was rearranged to N-acetyl-5-aminoindane **46** by phosphorous pentachloride at 0°C in 88% yield. Oxidation of compound **46** to N-acetyl-5-aminoindan-1-one **47** was accomplished by chromium trioxide in 69% yield. Thus, 5-aminoindan-1-one

48 was obtained in 64% yield from the hydrolysis of compound **47** with aqueous hydrochloric acid. 5-aminoindan-1-one **48** was diazotized with sodium nitrite and sulfuric acid to give the diazonium salt which was decomposed in aqueous cuprous cyanide solution to give 5-cyanoindan-1-one **49** in 83% yield.

Synthesis of methylated ketones

In general, indan-1-ones and tetralone were exhaustively methylated in dimethoxyethane with excess sodium hydride and methyl iodide under nitrogen atmosphere in dimethoxyethane (eq. 24). The yields of these methylated ketones are listed in Table 4.

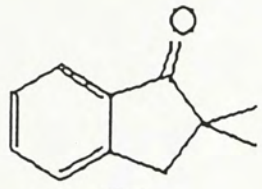
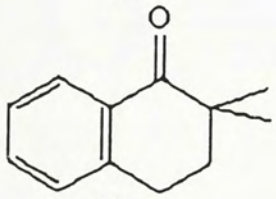
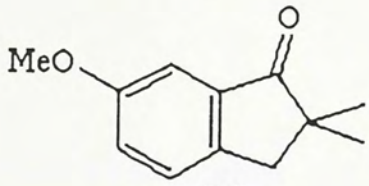
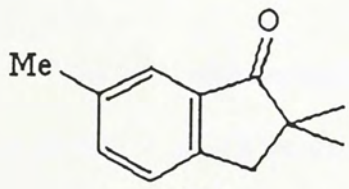
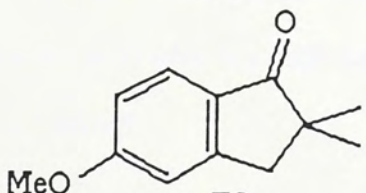
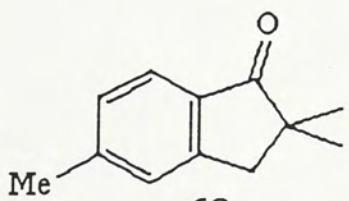
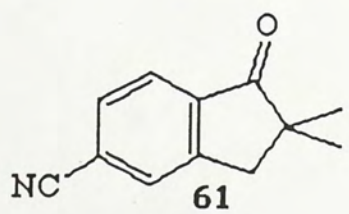


n = 1, X = H, 5-OMe, 5-Me, 5-CN, 6-OMe, 6-Me

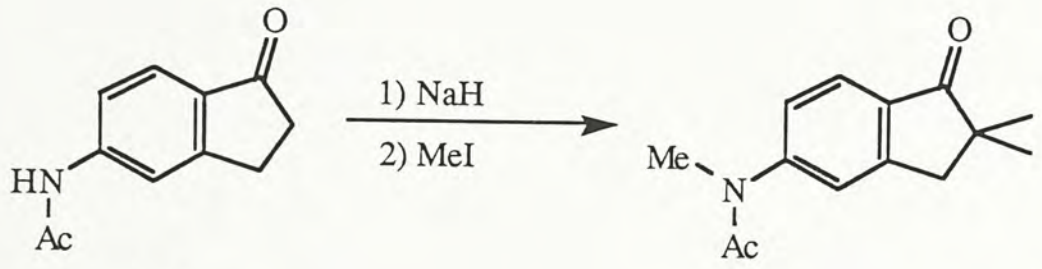
n = 2, X = H

(eq. 24)

Table 4: Preparation of methylated ketones

Compound	Yield (%)
 **55**	93
 **56**	81
 **57**	99
 **58**	75
 **59**	95
 **60**	85
 **61**	86

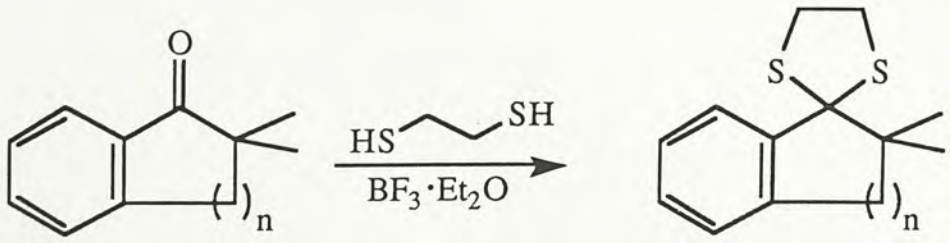
(N-Acetyl-N-methyl-5-amino)-2,2-dimethylindan-1-one **62** was directly obtained from the methylation of N-acetyl-5-aminoindan-1-one **47** with four equivalents of sodium hydride and methyl iodide (eq. 25).



47 **62** (eq. 25)

Synthesis of dithioacetals

Hindered dithioacetals were prepared by reacting the corresponding ketones with 1,2-ethanedithiol using boron trifluoride etherate as the catalyst for 2 h at 140°C (eq. 26). It is noted that no solvent should be used for this reaction! Otherwise, much longer reaction time was required and lower yields were normally observed. The result are complied in Table 5.



(eq. 26)

Table 5: Preparation of dithioacetals

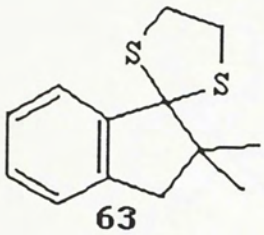
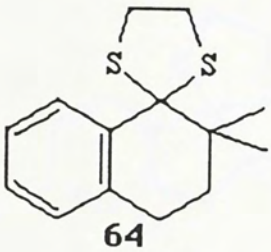
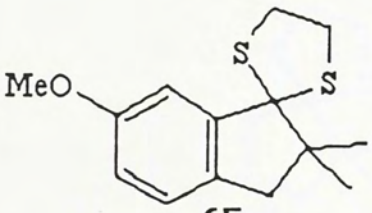
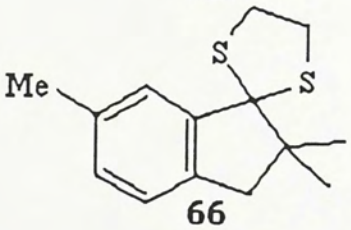
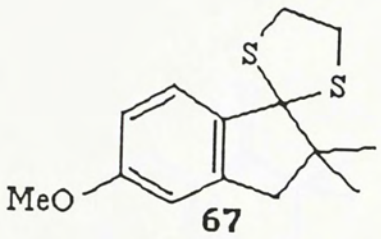
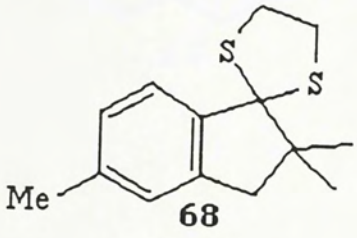
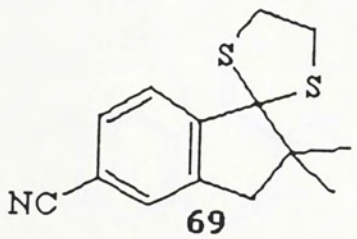
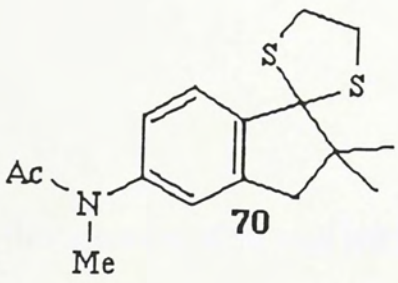
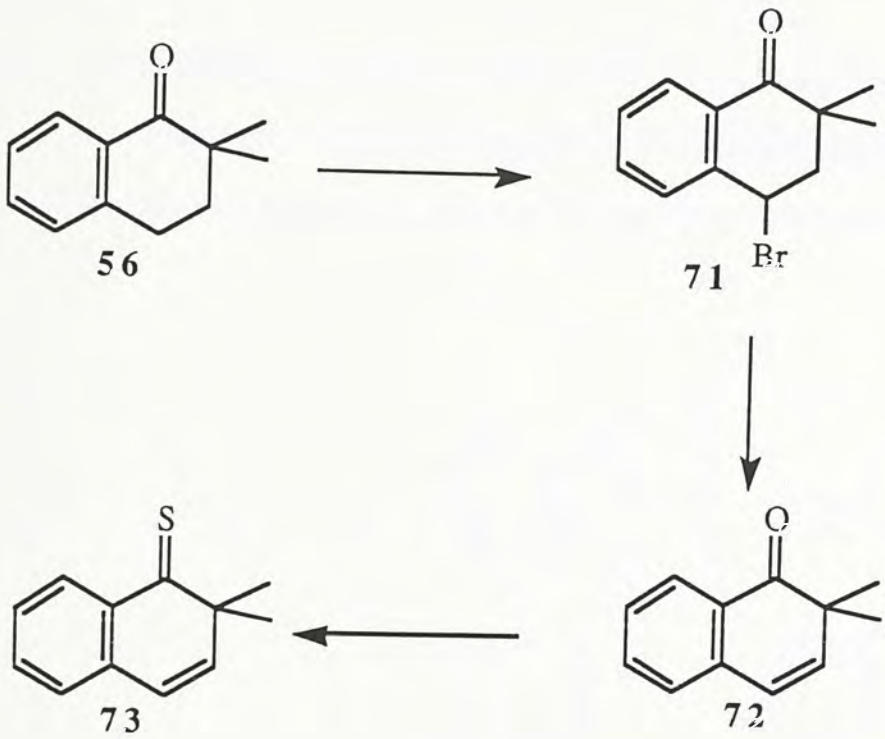
Compound	Yield (%)
 **63**	71
 **64**	77
 **65**	98
 **66**	66

Table 5 (Cont.)

Compound	Yield (%)
 **67**	83
 **68**	86
 **69**	92
 **70**	85

1,2-Dihydro-2,2-dimethylnapthalen-1-thione **73** was prepared according to Scheme 5.



Scheme 5

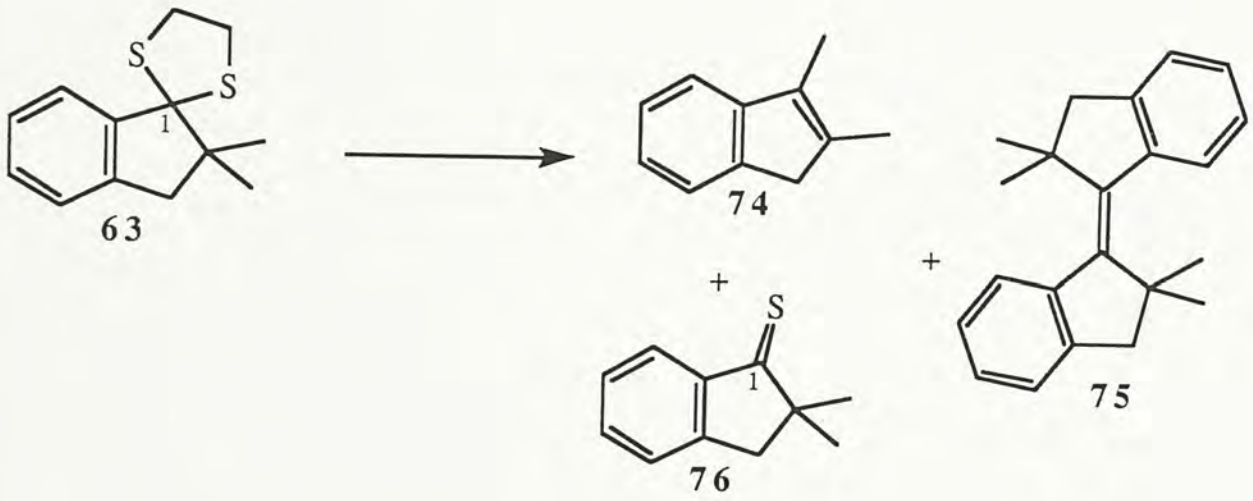
Bromination of **56** with NBS afforded compound **71** in 79% yield. Upon treatment with potassium t-butoxide **71** was converted to 1,2-dihydro-2,2-dimethylnapthalen-1-one **72** in 99% yield. Compound **73** was obtained in 91% yield from the reaction of **72** with phosphorous pentasulfide.

Desulfurization of dithioacetals using tungsten hexacarbonyl

In a typical procedure, a chlorobenzene solution of dithioacetal and 1.5 equivalents of tungsten hexacarbonyl was heated at 160°C under nitrogen atmosphere. The mixture turned into homogeneous as soon as the temperature was raised over 100°C. The colorless

solution slowly changed into yellow after it began to boil. Continued refluxing resulted in darkening of the mixture. The mixture was allowed to reflux for 8-24 h. After workup and chromatographic separation, the products were obtained.

Thus, the reaction of hindered dithioacetal 2,2-dimethyl-1,1-ethylenedithioindane **63** with tungsten hexacarbonyl for 18 h afforded a mixture of dimeric olefin **75** in addition to thione **76** and rearranged monomeric alkene **74** in 31%, 30% and 10% yields, respectively (eq. 27).



(eq. 27)

The structure for the thione was mainly proved by NMR spectroscopy. The ^{13}CNMR and ^{1}HNMR spectra of 2,2-dimethylindan-1-thione **76** are illustrated in Figure 1 and Figure 2.

The signal at low field (δ 254.7) in the ^{13}CNMR spectrum is assigned to the absorption of C_1 which clearly indicates the existence of a carbon sulfur double bond.[37] Moreover, the ^{1}HNMR spectrum is also consistent with the structure of the compound 2,2-dimethylindan-1-thione. Furthermore, treatment of **76** with lithium aluminum hydride afforded thiol **77** whose ^{1}HNMR spectrum is shown in Figure 3.

Figure 1: ^{1}HNMR spectrum of 2,2-dimethylindan-1-thione (**76**)

Figure 2: ^{13}CNMR spectrum of 2,2-dimethylindan-1-thione (**76**)

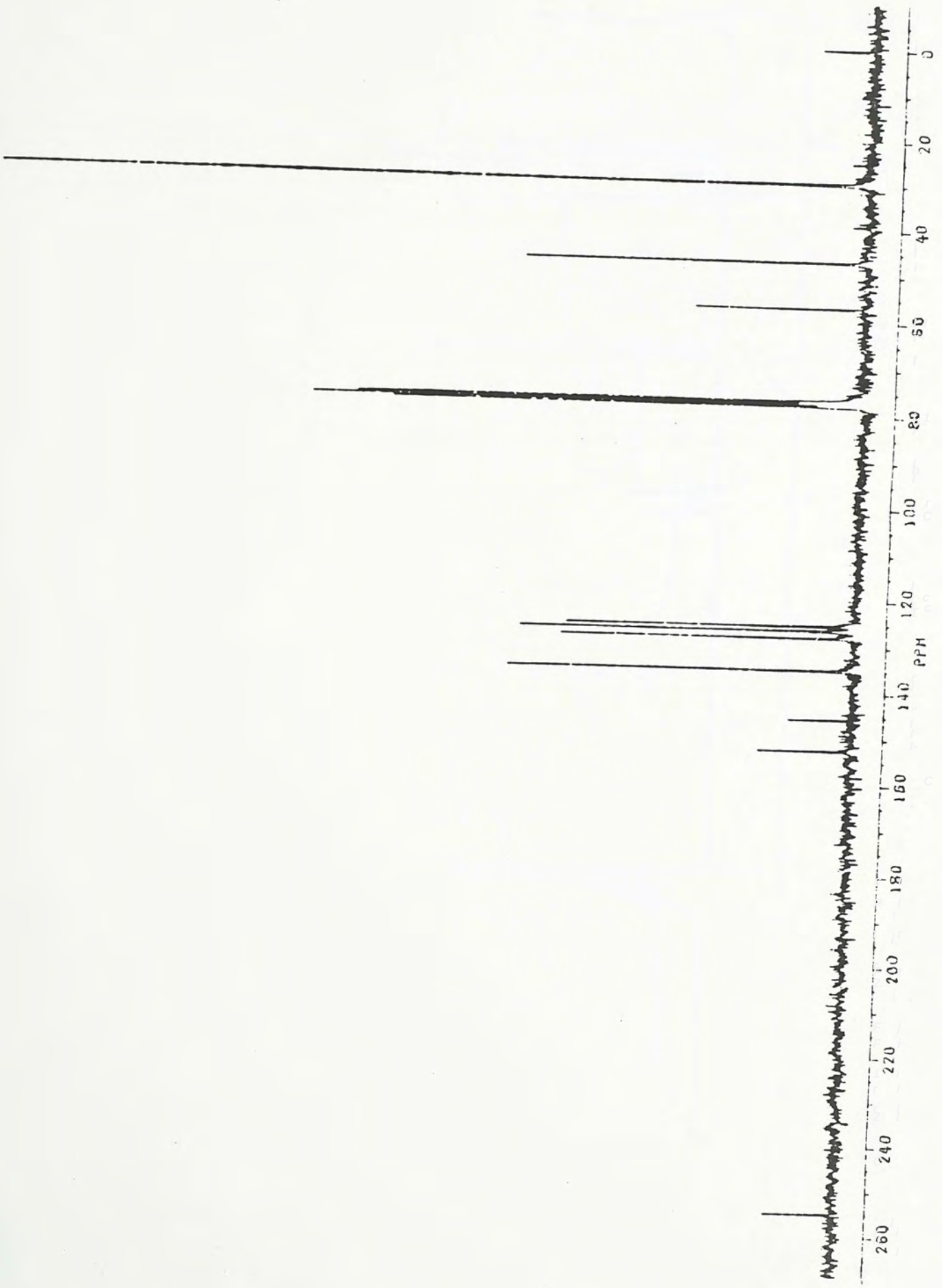
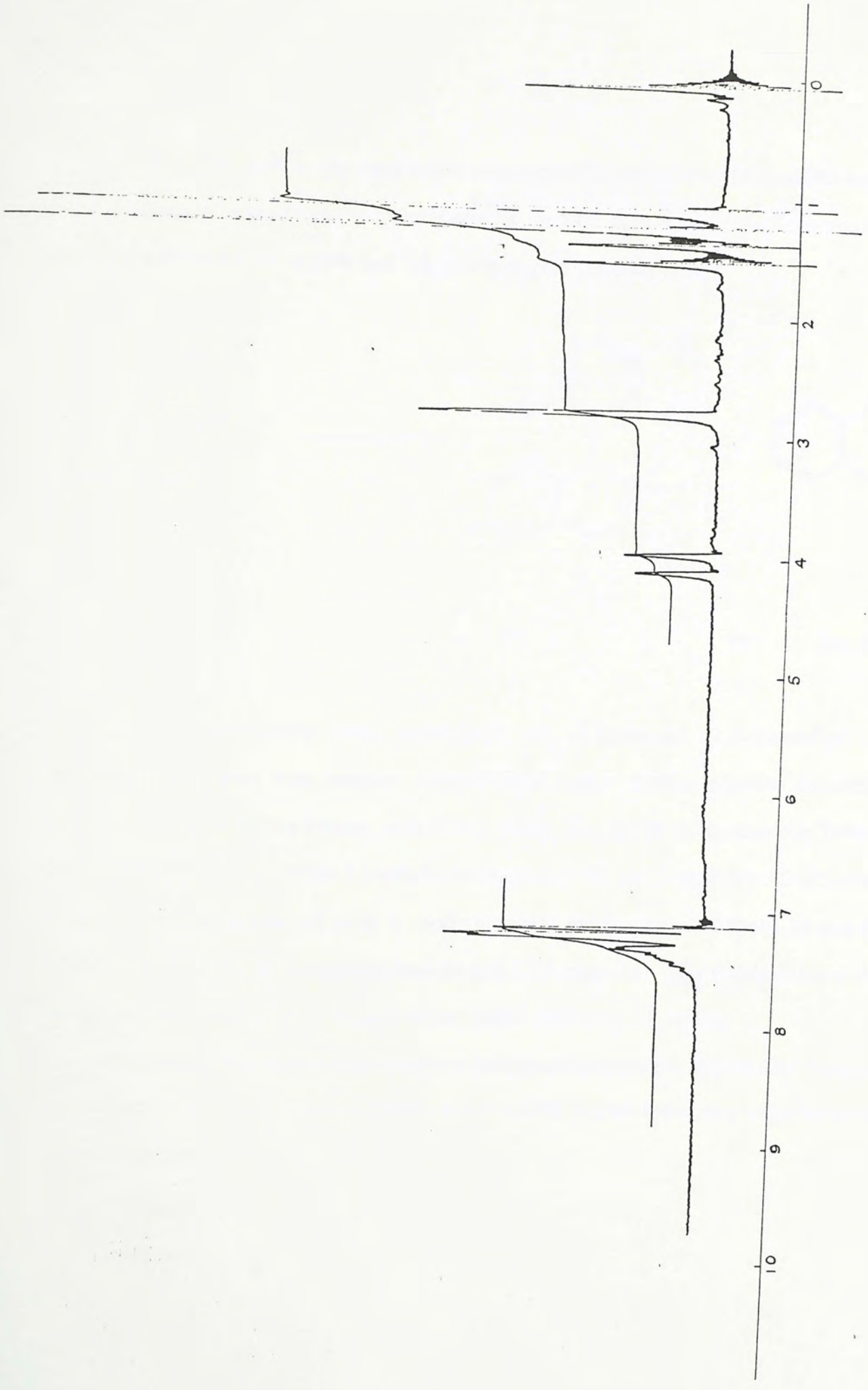
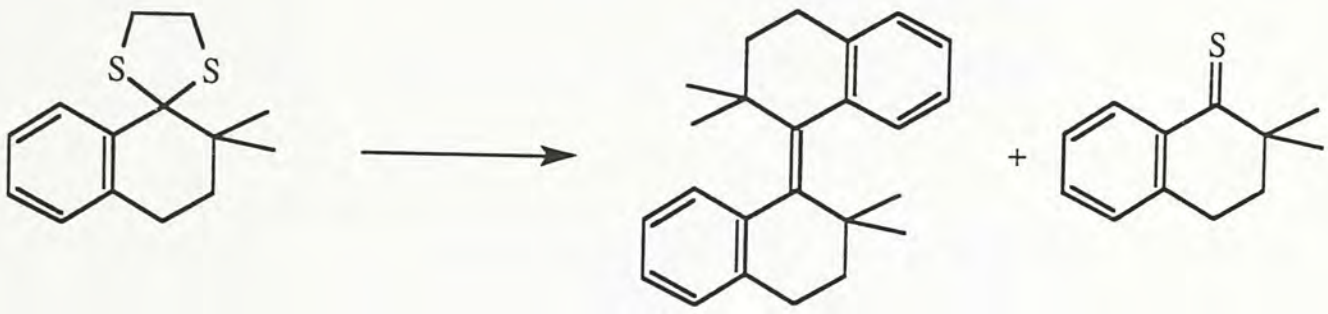


Figure 3: ^{1}HNMR spectrum of 2,2-dimethylindan-1-thiol (77)



In a similar manner, the desulfurdimerization of 2,2-dimethyl-ethylenedithiotetralin **64** with tungsten hexacarbonyl in chlorobenzene for 24 h gave a mixture of two products, dimer **78** and thione **79** in 15% and 9% yields respectively (eq. 28).



64 **78** **79** (eq. 28)

It is noteworthy that treatment of substituted 2,2-dimethyl-1,1-ethylenedithioindanes with tungsten hexacarbonyl under similar reaction conditions afforded the corresponding thiones in moderate yields. The results are tabulated in Table 6. Thus, 6-methoxy-2,2-dimethyl-1,1-ethylenedithioindane **65** and 5-methoxy-2,2-dimethyl-1,1-ethylenedithioindane **67** gave in moderate yield the respective thiones **80** and **82**. 2,2,6-Trimethyl-1,1-ethylenedithioindane **66** and 2,2,5-trimethyl-1,1-ethylenedithioindane **68**, on the other hand, gave in slightly better yields of thiones **81** and **83**.

In general, the reaction was somewhat substituent dependent. For electron donating substituents ($\sigma < 0$), the yields of thiones were slightly higher and shorter reaction times were normally required.

Table 6: The yield of **80-83** from the reaction of **65-68** with tungsten hexacarbonyl in chlorobenzene.

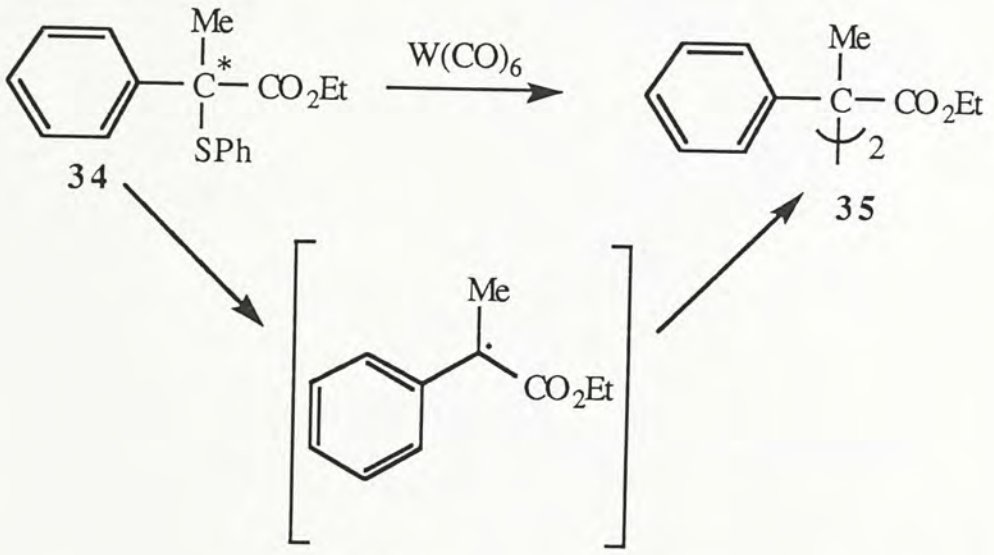
X	Reaction time (h)	% yield
6-OMe (**65**)	24	26
6-Me (**66**)	18	42
5-OMe (**67**)	8	36
5-Me (**68**)	8	38

Attempts to desulfurdimerize 5-cyano-2,2-dimethyl-1,1-ethylenedithioindane **69** and (N-acetyl-N-methyl-5-amino)-2,2-dimethyl-1,1-ethylenedithioindane **70** with tungsten hexacarbonyl in chlorobenzene for 48 h were not successful. Only starting materials **69** and **70** were recovered.

The formation of thioketones revealed an unprecedented type of the fragmentation of the dithiolane moiety. The gaseous product of the reaction was also carefully examined. Thus, the reaction of 2,2-dimethyl-1,1-ethylenedithioindane **63** was carried out in a closed system and any gas formed during the course of the reaction was introduced directly into a carbon tetrachloride solution of bromine. Three dibromoethane solutions in carbon

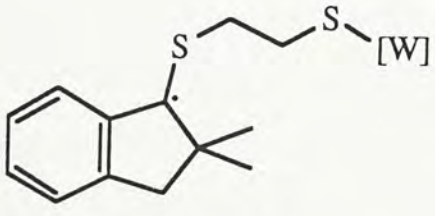
tetrachloride with different concentrations were prepared for calibrating the concentration of dibromoethane. By comparing integration of the methylene absorption of dibromoethane in ^{1}HNMR spectrum, the yield of dibromoethane was estimated to be 92%.

As mentioned previously, the desulfurization of thioether with tungsten hexacarbonyl in refluxing chlorobenzene occurs via a free radical mechanism (eq.29). The carbon-sulfur bond is cleaved homolytically to generate the radical intermediate.



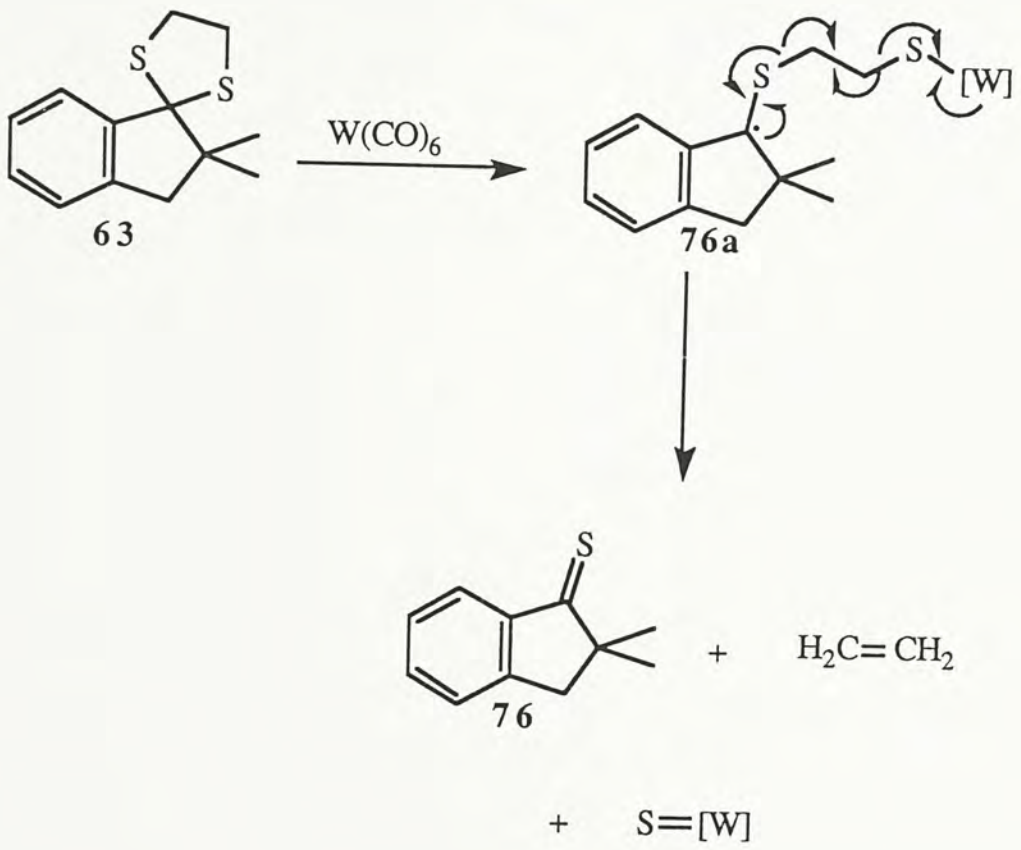
34 **35** **35a** (eq. 29)

On the basis of this argument, the reaction of dithioacetal with tungsten hexacarbonyl may occur via a similar pathway. The two carbon-sulfur bonds are cleaved at different stages. Thus, the radical intermediate **76a** is proposed.



76a

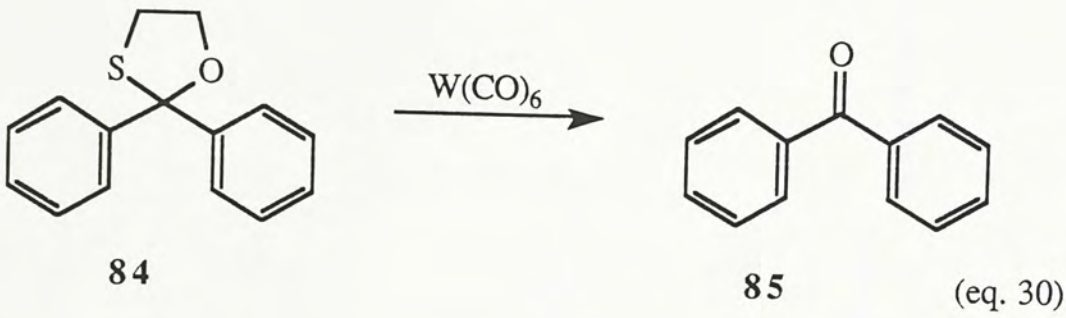
It may then undergo fragmentation to give thioketone **76** and ethene. A plausible mechanism is outlined in Scheme 6.



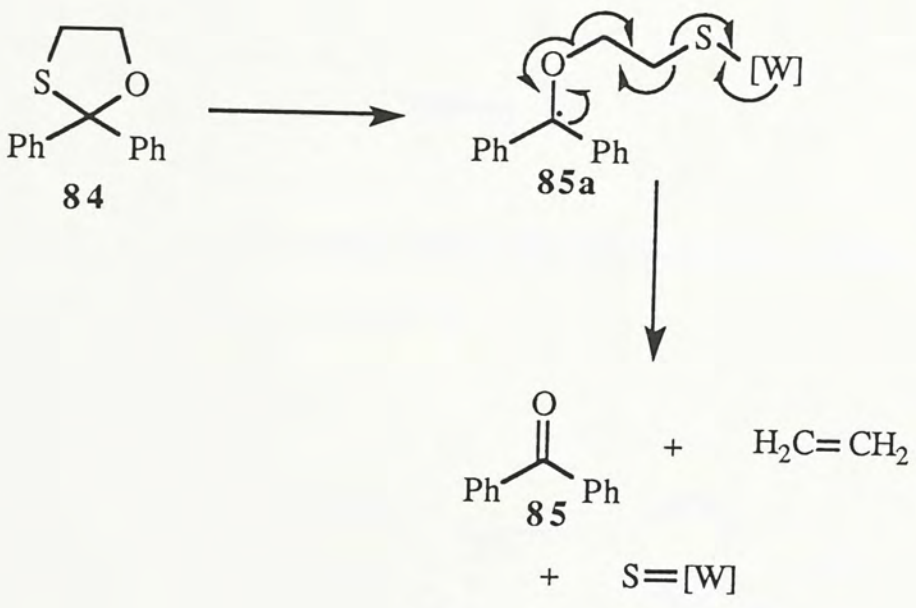
Scheme 6

It is understandable that the carbon-sulfur bond is generally weaker than the oxygen analog.[38] The carbon-sulfur bond cleavage is apparently more favorable than the breakage of the carbon-oxygen bond under the reaction conditions. Furthermore, group 6 metal carbonyl are thiophilic. If the above mechanism is correct, the thermolysis of oxthiolane in the presence of tungsten hexacarbonyl would yield the corresponding ketone via a similar fragmentation process (Scheme 7). Hence, treatment of **84** and tungsten hexacarbonyl in

refluxing chlorobenzene afforded **85** in 97% yield (eq. 30). Dibromoethane was estimated to be 62%.

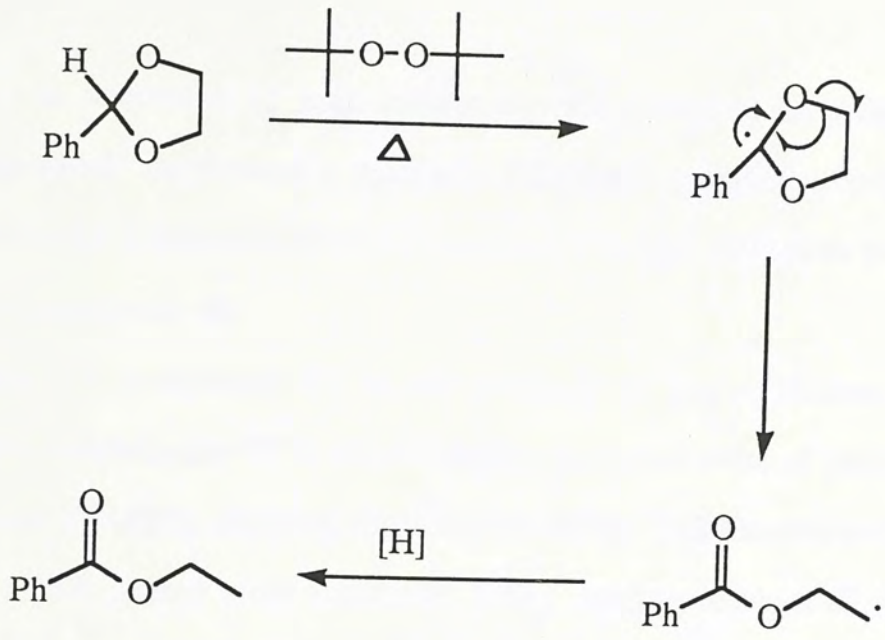


84 **85** (eq. 30)



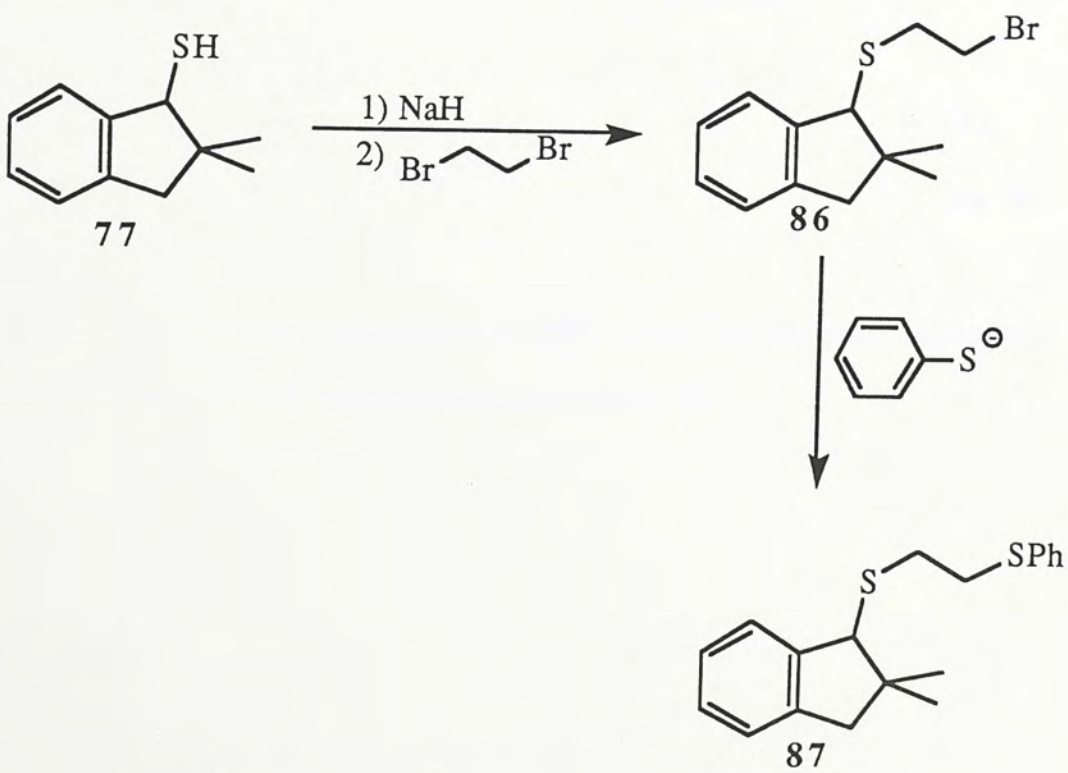
Scheme 7

It is noted that the fragmentation reactions of α-alkoxy-substituted radicals to yield a carbon-oxygen double bond are well-documented (Scheme 8).[39]



Scheme 8

In order to establish the radical intermediate in the overall reaction, thioether **87** was synthesized for comparison (Scheme 9).



Scheme 9

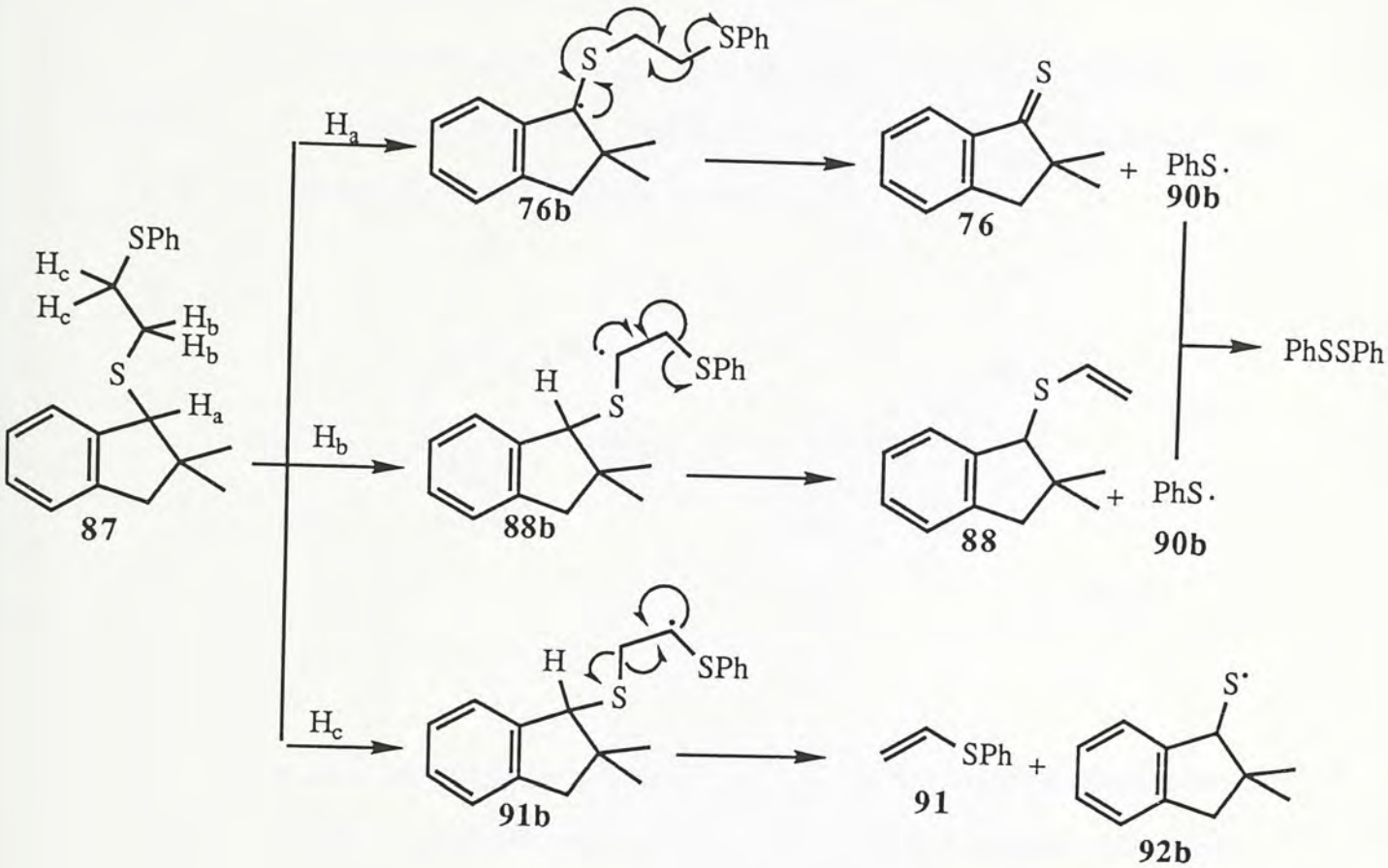
Treatment of mercaptan **77** with sodium hydride generated its corresponding sodium mercaptide which was allowed to react with 1,2-dibromoethane to afford the alkyl bromide **86** in 69% yield. Compound **87** was then prepared in 91% yield from the reaction of sodium thiophenoxide and **86**.

Thermolysis of compound **87** in the presence of one equivalent t-butyl adamantane-1-peroxycarboxylate **89** in chlorobenzene gave a mixtures of products, 2,2-dimethylindan-1-one **55** (42%), diphenyl disulfide **90** (34%), (2,2-dimethylindan-1-yl)-vinyl sulfide **88** (8%), phenyl vinyl sulfide **91** (3%), starting material **87** (35%) in addition to a trace amount of 2,2-dimethylindan-1-thione **76**. It is well-known that the thermal decomposition of **89** occurs via a free radical mechanism.[40]

89

(eq. 31)

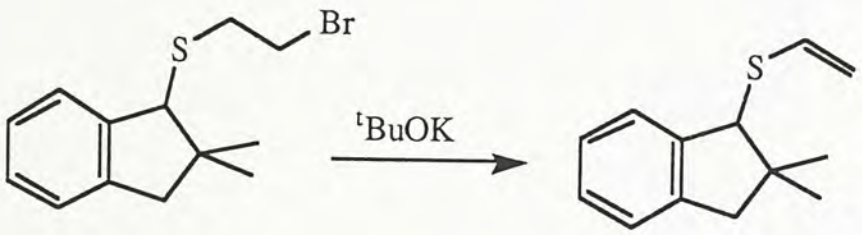
Adamantyl or t-butoxy radicals thus generated would abstract the hydrogens H_a, H_b or H_c from the compound **87** as summarized in Scheme 10.



Scheme 10

When H_a was abstracted, radical **76b** would be generated which may undergo fragmentation to give thione **76** and thiophenoxy radical **90b** which would dimerize to yield diphenyl disulfide **90**. Attempts to trap ethylene with bromine in carbon tetrachloride by a similar procedure described above were unsuccessful. Presumably, the radical species generated in situ may rapidly react with ethylene before escaping from the reaction mixture.[39] Radical **88b** was generated after the abstraction of H_b which may also undergo similar fragmentation to yield (2,2-dimethylindan-1-yl)-vinyl sulfide **88** and thiophenoxy radical **90b**. Similarly, phenyl vinyl sulfide **91** and **92b** may be formed from the fragmentation of radical **91b** after the abstraction of H_c. **92b** may further react under the reaction conditions to afford **55**.

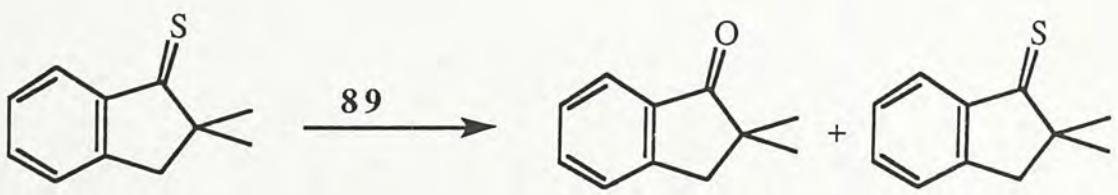
Vinyl sulfide **88** was synthesized by elimination of alkyl bromide **86** with t-butoxide (eq. 32). The compound prepared in this way was identical in every respect with the sample obtained from the thermolysis of compound **87**.†



86 **88** (eq. 32)

The observation on the radical-initiated reaction of **87** is compatible with that on the tungsten hexacarbonyl-mediated fragmentation of **63**. As a result, it seems plausible that the latter reaction proceeds via a similar radical mechanism shown in Scheme 6.

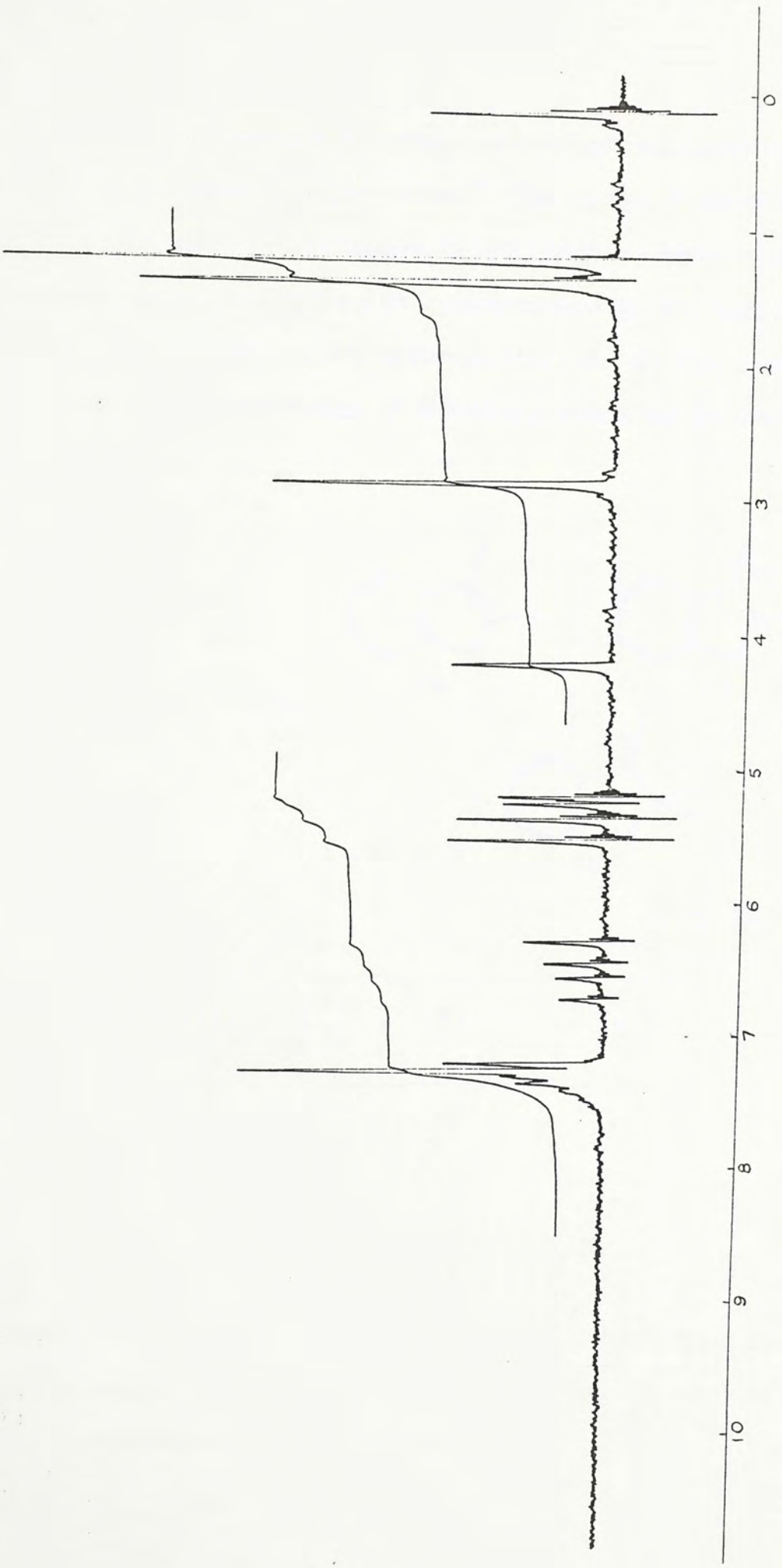
It is noteworthy that thione **76** was unstable under these conditions. Treatment of **76** with one equivalent of **89** in refluxing chlorobenzene gave a mixture of ketone **55** and starting material **76** in 65% and 33% yields respectively (eq. 33). Thus, in situ oxidation of **76** to **55** may occur during the course of reaction of **87** with **89**.



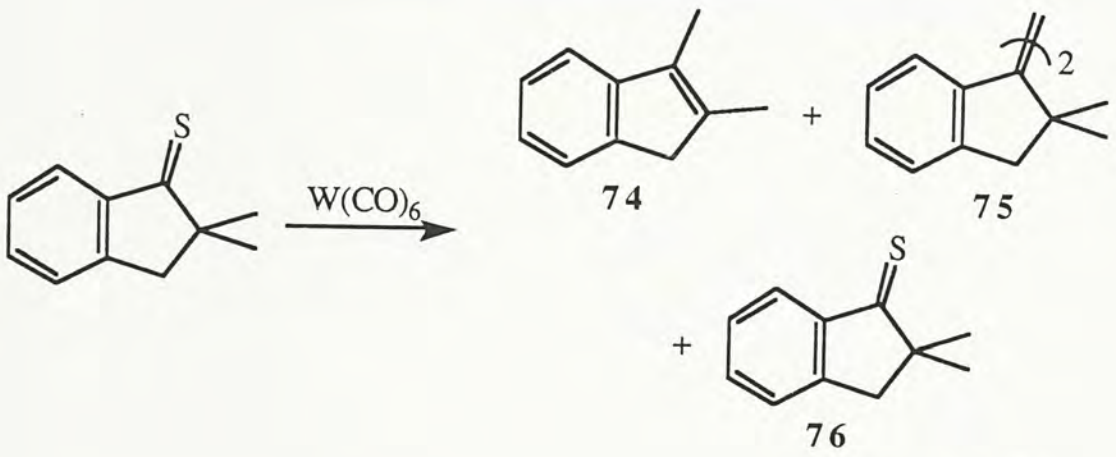
76 **55** **76** (eq. 33)

† Compound **87** was decomposed into ethanal and others products in deuteriochloroform solution for 24 h.

Figure 4: ^{1}HNMR spectrum of 2,2-dimethylindan-1-yl vinyl sulfide (88)



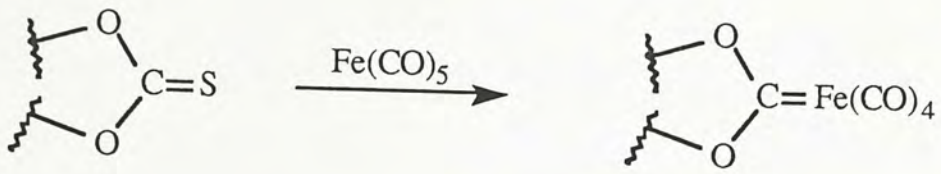
As mentioned in the introduction, thioketones can desulfurdimerize upon treatment with manganese or cobalt carbonyls to give olefins.[23] The reaction of thione **76** with tungsten hexacarbonyl in refluxing chlorobenzene for 24 h also gave a mixture of dimeric olefin **75** and starting material **76** in 24% and 65% yields respectively. Prolonged heating for 72 h afforded **74** and **75** in 34% and 19% yieldsrespectively (eq. 34). This observation further supports that desulfurdimerization of dithioacetal occurs via the thioketone intermediate.



(eq. 34)

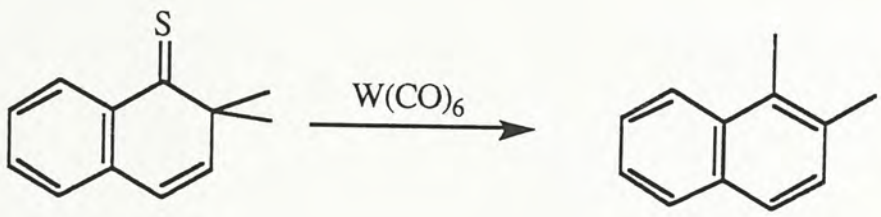
Time (h)	% Yield of **74**	**75**	**76**
24	0	24	65
72	34	19	0

The actual mode of the conversion of thioketone into dimeric olefin is not clear. A metallocarbene intermediate is envisaged. Indeed, when thiocarbonate is treated with iron carbonyl, an iron carbene complex **93** was isolated (eq. 35).[41]



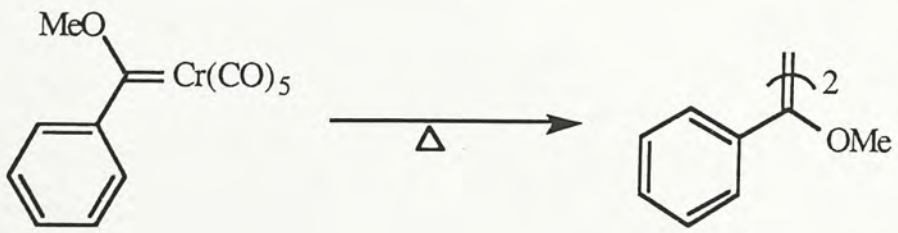
93 (eq. 35)

As mentioned above, **74** was obtained in significant amount from the reaction of thione **76** and dithioacetal **63** with tungsten hexacarbonyl. Furthermore, the reaction of thione **73** under similar conditions afford **92** exclusively in 45% yield (eq. 36).

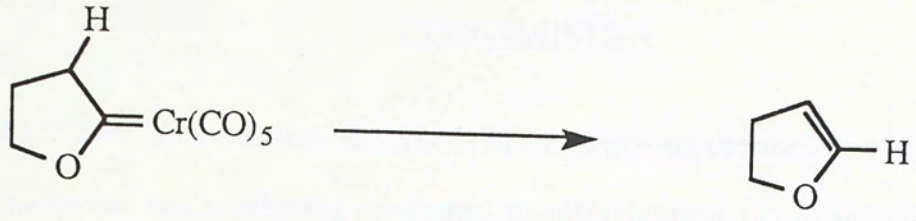


73 **92** (eq. 36)

It is noted that the thermal decomposition of the carbene complex lead to the corresponding dimer (eq. 37).[42] Insertion is another common reaction of metallocarbenes (eq 38).[43]



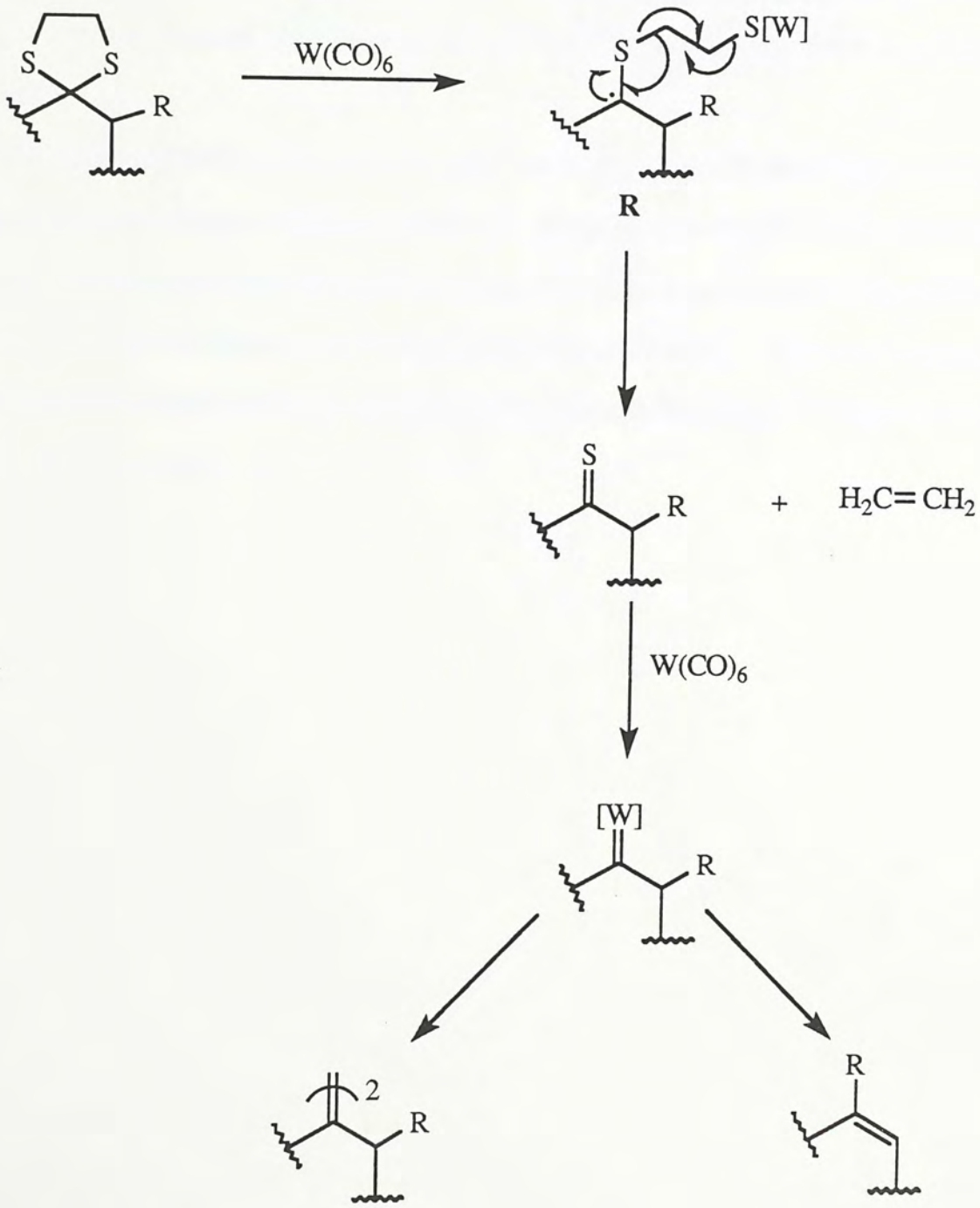
94 **95** (eq. 37)



96 **97** (eq. 38)

CONCLUSION

Based on the evidences described in the previous sections, a plausible mechanism for the tungsten hexacarbonyl mediated desulfurization of dithioacetals is proposed (Scheme 11)



Scheme 11

Upon thermolysis, one of the carbon-sulfur bonds in dithioacetal is cleaved to generate the radical **R**. It may undergo fragmentation to give ethene and thione. The thione may react with tungsten hexacarbonyl to form a metallocarbene species which may dimerize leading to the formation of the dimeric olefin or undergo insertion reaction to generate monomeric alkene.

Although the yields of the thiones may not be high enough for general synthetic applications, the mechanistic studies and tungsten mediated carbon-sulfur bond cleavage[33] do suggest the reaction occurs via radical mechanism. Furthermore, a novel fragmentation of dithioacetals giving thiones and ethene has been uncovered. The overall process suggests that dithioacetal can serve as a carbene synthon and the reverse reaction shown in eq. 16 is hence solidified.

EXPERIMENTAL SECTION

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Proton nuclear magnetic resonance (^{1}HNMR) spectra were obtained on a JEOL PMX-60 (60 MHz) NMR spectrometer and/or a Bruker WM250 (250 MHz) NMR spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units. Coupling constants are in hertz (Hz). ^{1}HNMR data are reported in this order: chemical shift; multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad); coupling constant (s); number (s) of proton(s). Unless otherwise specified, deuteriochloroform was used as the solvent. ^{13}CNMR spectra were recorded on a Bruker WM250 spectrometer operating at 62.5 MHz. Peak positions are on δ scale when using deuteriochloroform of δ 77.0 as internal standards. Mass spectral (MS) data were obtained on a VG 7070F mass spectrometer. Fragmentation data are reported as m/z. Elemental analyses were performed at the Department of Chemistry, National Taiwan University. Reagent-grade tungsten hexacarbonyl (Aldrich or Fluka) was used without further purification. Chromatographic separation was performed on silica gel (Merck, 70-230 mesh). Flash chromatographic separation was performed on silica gel (Merck, 230-400 mesh). All solvents were purified by standard procedure prior to use.[44] Chlorobenzene was distilled from calcium hydride and stored over molecular sieve (4Å).

p-Methoxycinnamic acid (36) A solution of anisaldehyde (45.0 g, 0.33 mol), malonic acid (75.0 g, 0.72 mol) and piperidine (2.5 mL) in pyridine (150 mL) was refluxed for 2 h. The reaction mixture was cooled and poured into ice water. Hydrochloric acid (20%) was added to neutralized the reaction mixture. White precipitate was filtered, washed with water to afford the crude product which recrystallized from glacial acetic

acid to give p-methoxycinnamic acid (**36**) (57.0 g, 96%); m.p. 172-173°C (lit.[45] 174°C); ^{1}HNMR δ 3.83 (s, 3H), 5.50 (br, 1H), 6.30 (d, J = 12 Hz, 1H), 6.83-7.63 (m, 4H), 7.73 (d, J = 12 Hz, 1H); m/z 178 (M^+).

p-Methylcinnamic acid (37) Via the same procedure as described above, p-methylbenzaldehyde (40.0 g, 0.33 mol), malonic acid (75.0 g, 0.72 mol) and piperidine (2.5 mL) in pyridine (150 mL) was refluxed for 2 h to give the crude acid which recrystallized from chloroform to afford p-methylcinnamic acid (**37**) (48.0 g, 90%); m.p. 197-198°C (lit.[46] 198-199°C); ^{1}HNMR δ 2.36 (s, 3H), 6.4 (d, J = 12 Hz, 1H), 7.07-7.60 (m, 4H), 7.80 (d, J = 12 Hz, 1H); m/z 162 (M^+).

m-Methoxycinnamic acid (38) According to the same procedure as described above, m-methoxybenzaldehyde (45.0 g, 0.33 mol) , malonic acid (75.0 g, 0.72 mol) and piperidine (2.5 mL) in pyridine (150 mL) was refluxed for 2 h to give the crude acid which recrystallized from ethanol to yield m-methoxycinnamic acid (**38**) (45.0 g, 84%); m.p. 119-120°C (lit.[47] 120°C); ^{1}HNMR δ 3.80 (s, 3H), 6.43 (d, J = 12 Hz, 1H), 6.8-7.40 (m, 4H), 7.77 (d, J = 12 Hz, 1H); m/z 178 (M^+).

m-Methylcinnamic acid (39) A mixture of 3-bromotoluene (17.0 g, 0.1 mol), acrylic acid (8.0 g, 0.11 mol), tri-n-butylamine (53.0 g, 0.22 mol), palladium acetate (0.22 g, 1 mol%) was heated at 120°C under nitrogen atmosphere. After the mixture had turned dark, heating was continued for about 2 h. The mixture was then poured into aqueous sodium hydroxide (10%, 50 mL) and washed with ether. The aqueous phase was then acidified with hydrochloric acid (20%). The precipitate was filtered, washed thoroughly with water and dried under vacuum to afford the crude acid which recrystallized from ethanol to give m-methylcinnamic acid (**39**) (13.0 g, 79%); m.p.114-115°C (lit.[48] 115°C);

^{1}HNMR δ 2.02 (s, 3H), 6.61 (d, J = 12 Hz, 1H), 7.13-7.46 (m, 4H), 7.92 (d, J = 12 Hz, 1H), 9.5 (br, 1H); m/z 162 (M^+).

3-(4-Methoxyphenyl)propionic acid (40) A slurry of p-methoxycinnamic acid (18.0 g, 0.10 mol) and a catalytic amount of Pd/C (10%) in absolute ethanol (150 mL) was subjected to a Parr hydrogenation flask. Under hydrogen atmosphere (50 psi), it was shaken until no further hydrogen was absorbed (ca. 12 h). It was then filtered and the filtrate was evaporated in vacuo. The residue was recrystallized from ethanol to give 3-(4-methoxyphenyl)propionic acid (**40**) (18.0 g, 99%); m.p. 99-101°C (lit.[48] 104-105°C); ^{1}HNMR δ 2.77 (m, 4H), 3.76 (s, 3H), 6.78-7.05 (m, 4H); m/z 180 (M^+), 121 (base peak).

3-(4-Methylphenyl)propionic acid (41) Via the same procedure as describe above, p-methylcinnamic acid (16.0 g, 0.10 mol) was hydrogenated to give 3-(4-methylphenyl)propionic acid (**41**) (16.0 g, 98%); m.p. 118-119°C (lit.[49] 120°C); ^{1}HNMR δ 2.30 (s, 3H), 2.43-3.10 (m, 4H), 7.07 (s, 4H), 8.50 (br, 1H); m/z 164 (M^+), 105 (base peak).

3-(3-Methoxyphenyl)propionic acid (42) Via the same procedure as described above, m-methoxycinnamic acid (18 g, 0,101 mol) was allowed to hydrogenated to afford 3-(3-methoxyphenyl)propionic acid (**42**) (17.6 g, 98%); m.p. 49-50°C (lit.[50] 51°C); ^{1}HNMR δ 2.46-3.17 (m, 4H), 3.77 (s, 3H), 6.63-7.40 (m, 4H), 9.1 (br, 1H); m/z 180 (M^+).

3-(3-Methylphenyl)propionic acid (43) By employing the same procedure as describe above, m-methylcinnamic acid (16.0 g, 0.10 mol) was transformed into 3-(3-methylphenyl)propionic acid (**43**) (16.2 g, 99%); m.p. 41-42°C (lit.[49] 42-43°C); ^{1}HNMR

δ 2.30 (s, 3H), 2.80 (m, 4H), 6.83-7.33 (m, 4H), 10.20 (br, 1H); m/z 164 (M^+), 105 (base peak).

5-Acetylindane (44) According to the literature procedure[51] with modification, aluminum chloride (100 g, 0.75 mol) and acetyl chloride (58 g, 0.74 mol) were dissolved in dichloromethane (800 mL) to which was added dropwise indane (80 g, 0.68 mol) in dichloromethane (100 mL). The solution was stirred at room temperature for 15 min and quenched with concentrated hydrochloric acid in ice. Organic layer was separated and the aqueous solution was extracted with dichloromethane. The combined organic layers were washed with aqueous potassium hydroxide (5%, 200 mL), water (200 mL), dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated in vacuo and the residue was distilled to give 5-acetylindane (44) (98.7 g, 91%); b.p. 109°C (0.2 mm) (lit.[51] 142°C, 15 mm); ^{1}HNMR δ 2.13 (m, 2H), 2.53 (s, 3H), 2.93 (t, 4H), 7.13-7.87 (m, 3H); m/z 160 (M^+).

Oxime of 5-acetylindane (45) A mixture of 5-acetylindane (98 g, 0.61 mol), hydroxylamine hydrochloride (70 g, 0.10 mol) and sodium acetate (150 g, 1.83 mol) in ethanol (500 mL, 60%) was refluxed overnight. After being cooled to room temperature, the oxime (45) (91 g, 84%) was precipitated and collected by filtration. The solid was used for the next operation without further purification; m/z 175 (M^+).

N-acetyl-5-aminoindane (46) Oxime of 5-acetylindane (12.0 g, 0.069 mol) was added in portions to a solution of phosphorus pentachloride (9.0 g, 0.043 mol) in dry ether (40 mL) at 0°C. The reaction mixture was stirred for 2 h, quenched with water (50 mL) and then extracted with ether. The combined organic layers were washed twice with aqueous potassium hydroxide (5%, 50 mL), water (50 mL), dried over anhydrous

magnesium sulfate, filtered and the filtrate was evaporated in vacuo to obtain the crude product which recrystallized from ethanol to yield N-acetyl-5-aminoindane (46) (10.5 g, 88%); m.p.106-107°C (lit.[51] 106°C); ^{1}HNMR δ 2.07 (m, 2H), 2.13 (s, 3H), 2.87 (t, 4H), 7.10-7.47 (m, 3H), 7.70 (br, 1H); m/z 175 (M^+).

N-acetyl-5-aminoindan-1-one (47) To a solution of N-acetyl-5-aminoindane (7.0 g, 0.04 mol) in acetic acid (18 mL) and acetic anhydride (5.23 mL) cooled in an ice-bath was added dropwise a solution of chromium trioxide (5.23 g, 0.0523 mol) in water (3.92 mL) and acetic acid (15.7 mL) while keeping the reaction temperature below 10°C. The mixture was stirred at room temperature overnight and then poured into ice-water. It was then filtered and dried to give the residue which recrystallized from ethanol to yield N-acetyl-5-aminoindan-1-one (**47**) (5.2 g, 69%); m.p.167-168°C (lit.[36] 170-171°C); ^{1}HNMR δ 2.2 (s, 3H), 2.53-2.80 (m, 2H), 3.00-3.23 (m, 2H), 7.07-8.07 (m, 3H), 7.83 (br, 1H); m/z 189 (M^+).

5-aminoindan-1-one (48) N-acetyl-5-aminoindan-1-one (15.1 g, 0.080 mol) in hydrochloric acid (200 mL, 0.8M) and was refluxed for 1 h. After being cooled to room temperature, the reaction mixture was neutralized with aqueous sodium hydroxide (10%). The precipitate was filtered which recrystallized from ethanol to give 5-aminoindan-1-one (**48**) (7.0 g, 64 %); m.p. 186-187°C (lit.[36] 186.5-187°C); ^{1}HNMR δ 2.47-2.73 (m, 2H), 2.87-3.17 (m, 2H), 4.20 (br, 2H), 6.43-6.67 (m, 2H), 7.43-7.67 (m, 1H); m/z 147 (M^+).

5-Cyanoindan-1-one (49) To a solution of copper (II) sulfate (10.0 g, 0.041 mol) and sodium chloride (2.7 g, 0.046 mol) in water (50 mL) was added a solution of sodium bisulfite (2.1 g, 0.0202 mol) and sodium hydroxide (1.0 g, 0.025 mol) in water (25 mL) with stirring. After being cooled to room temperature, the supernatant was decanted and the residue was washed with water . Water (25 mL) was then added to which a solution of

potassium cyanide (7 g, 0.11 mol) in water (20 mL) was introduced with stirring and the mixture was cooled in an ice-bath.

To a solution of 5-aminoindan-1-one (4.2 g, 0.029 mol) in hydrochloric acid (15%, 17 mL) was added dropwise a solution of sodium nitrite (2.1 g, 0.030 mol) in water (5 mL) while keeping the temperature below 5°C. After the addition was completed, the solution was neutralized with solid sodium carbonate while keeping the temperature below 5°C by the addition of ice to the mixture. The solution was then added slowly to a mixture of the cuprous cyanide solution prepared above and toluene (10 mL). The mixture was allowed to warm to room temperature and then heated at 50°C for 1 h. The solution was cooled and orange precipitate was filtered, washed with water and recrystallized from ethanol to give 5-cyanoindan-1-one (**49**) (4.0 g, 83%); m.p. 130-131°C (lit.[36] 130-131°C); ^{1}HNMR δ 2.60-2.90 (m, 2H), 3.07-3.37 (m, 2H), 7.37-8.00 (m, 3H); m/z 157 (M^+), 129 (base peak).

6-methoxyindan-1-one (50) 3-(4-methoxyphenyl)propionic acid (3.0 g, 0.017 mol) and phosphorus pentachloride (3.6 g, 0.017 mol) were mixed with shaking until no more hydrogen chloride was evolved. The mixture was evacuated under aspirator pressure at 80-90°C for 20 min. The residue acid chloride was dissolved in dry, thiophene free benzene (70 mL) in a flame-dried flask. The solution was immersed in salt ice-bath just to the solidification point of benzene and aluminum chloride (2.3 g, 0.017) was added in portions over a period of fifteen min. After stirring for 3.5 h at room temperature, the dark-red solution was decomposed with a mixture of ice and concentrated hydrochloric acid. The benzene layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with potassium hydroxide (2%) containing sodium chloride, dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated in vacuo to afford the residue which recrystallized from ethanol to yield 6-

methoxyindan-1-one (**50**) (2.0 g, 74%); m.p. 108-109°C (lit.[52] 108-109°C); ^{1}HNMR δ 2.50-2.83 (m, 2H), 2.93-3.20 (m, 2H), 3.80 (s, 3H), 7.00-7.37 (m, 3H); m/z 162 (M^+).

6-methylindan-1-one (51) 3-(4-methylphenyl)propionic acid (2.4 g, 0.017 mol) and phosphorus pentachloride (3.6 g, 0.017 mol) were mixed with shaking until no hydrogen chloride was evolved. The mixture was evacuated under aspirator pressure at 80-90°C for 20 min. The residue acid chloride in dichloromethane (10 mL) was added dropwise to a solution containing aluminum chloride (2.3 g, 0.017 mol) in dichloromethane (50 mL). After stirring at room temperature for 1 h, the dark red solution was decomposed with a mixture of ice and concentrated hydrochloric acid. The dichloromethane layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with potassium hydroxide (2%, 50 mL) containing sodium chloride, dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated in vacuo to afford the residue which recrystallized from ethanol to give 6-methylindan-1-one (**51**) (1.90 g, 64%); m.p. 62-63°C (lit.[53] 64-65°C); ^{1}HNMR δ 2.40 (s, 3H), 2.53-2.80 (m, 2H), 2.97-3.27 (m, 2H), 7.33-7.63 (m, 3H); m/z 146 (M^+).

5-methoxyindan-1-one (52) 3-(3-methoxyphenyl)propionic acid (2.0 g, 0.011 mol) was allowed to react with a mixture containing phosphorous pentaoxide (12 g, 0.085) and phosphoric acid (8 g, 0.082 mol) at 90°C for 1 h. The resulting mixture was allowed to cool and was hydrolyzed by pouring into ice-water for 30 min. The aqueous mixture was extracted with two portions of ether. The combined organic layers were washed successively with water, aqueous acetic acid (3%, 30 mL), sodium bicarbonate solution (5%, 30 mL) and again with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to give the residue which recrystallized from ethanol to yield 5-methoxyindan-1-one (**52**) (1.6 g, 80%); m.p. 107-108°C (lit.[54]

111°C); ^{1}HNMR δ 2.47-2.80 (m, 2H), 2.90-3.20 (m, 2H), 3.83 (s, 3H), 6.73-7.00 (m, 2H), 7.57-7.80 (m, 1H); m/z 162 (M^+).

5-methylindan-1-one (53) and 7-methylindan-1-one (54) 3-(3-methylphenyl)propionic acid (2.4 g, 0.017 mol) and phosphorus pentachloride (3.6 g, 0.017 mol) were mixed with shaking until no more hydrogen chloride was evolved. To a solution containing aluminum chloride (2.3 g, 0.017 mol) in dichloromethane (50 mL) was added dropwise a solution of acid chloride in dichloromethane (10 mL) while keeping the reaction temperature at 0°C. The reaction mixture was stirred for 1 h at room temperature and then poured into a mixture of ice and concentrated hydrochloric acid. The combined organic layer was washed with potassium hydroxide (2%, 50 mL) containing sodium chloride, dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated in vacuo to afford the residue which recrystallized from ethanol to give 5-methylindan-1-one (**53**) (1.15 g, 47%); m.p. 65-67°C (lit.[55] 65°C); ^{1}HNMR δ 2.40 (s, 3H), 2.53-2.83 (m, 2H), 2.97-3.03 (m, 2H), 7.03-7.77 (m, 3H) and 7-methylindan-1-one (**54**) (1.15 g, 47%); m.p. 50-51°C (lit.[56] 54-55°C); ^{1}HNMR δ 2.50-2.83 (m, 2H), 2.63 (s, 3H), 2.93-3.30 (m, 2H), 7.0-7.57 (m, 3H).

General procedure for synthesizing methylated ketones. A solution of ketone (10 mmol) in dimethoxyethane (10 mL) was added dropwise to a slurry containing sodium hydride (80%, 0.90 g, 30 mmol) in dimethoxyethane (20 mL) under nitrogen atmosphere. The mixture was stirred for 5 min and methyl iodide (2 mL, 30 mmol) in dimethoxyethane (5 mL) was added over a period of 5-15 min. After stirring for 15 min to 18 h, water (40 mL) was added and the mixture was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo. The residue was purified by chromatography on silica gel or by distillation to give the desired product.

2,2-Dimethylindan-1-one (55) According to the general procedure, a mixture of indan-1-one (1.32 g, 10 mmol), sodium hydride (80%, 0.90 g, 30 mmol) and methyl iodide (2.0 mL, 30 mmol) was treated for 1 h at room temperature to give 2,2-dimethylindan-1-one (**55**) (1.50 g, 93%); b.p. 67°C (0.2 mm, Kugelrohr) which solidified on standing; m.p. 43-44°C (lit.[57] m.p. 42-43°C) ; ^{1}HNMR δ 1.23 (s, 6H), 3.00 (s, 2H), 7.14-7.87 (m, 4H); m/z 160 (M^+), 145 (base peak).

2,2-Dimethyltetra-1-one (56) Via the general procedure, a mixture of tetra-1-one (1.46 g, 10 mmol), sodium hydride (80%, 0.90 g, 30 mmol) and methyl iodide (2.0 mL, 30 mmol) was stirred for 2 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane-ethyl acetate (10:1) to give 2,2-dimethyltetra-1-one (**56**) (1.40 g, 81%); b.p. 70°C (0.2 mm, Kugelrohr) (lit.[58] 145°C, 20 mm); ^{1}HNMR δ 1.20 (s, 6H), 2.00 (m, 2H), 3.00 (m, 2H), 7.10-7.53 (m, 3H), 7.97-8.17 (dd, J = 2, 8 Hz, 1H); m/z 174 (M^+), 118 (base peak).

2,2-Dimethyl-6-methoxyindan-1-one (57) By employing the same method as described in the general procedure, a dimethoxyethane solution (35 mL) of 6-methoxyindan-1-one (1.30 g, 8.0 mmol), sodium hydride (80%, 0.72 g, 24 mmol) and methyl iodide (2.0 mL, 30 mmol) was stirred overnight at room temperature to yield 2,2-dimethyl-6-methoxyindan-1-one (**57**) as colorless liquid (1.50 g, 99%); b.p. 96°C (0.2 mm, Kugelrohr); ^{1}HNMR δ 1.23 (s, 6H), 2.93 (s, 2H), 3.87 (s, 3H), 7.15 (d, J = 8 Hz, 1H), 7.29 (d, J = 8 Hz, 1H), 7.40 (s, 1H); m/z 190 (M^+), 175 (base peak); accurate mass calcd for $C_{12}H_{14}O_2$: 190.0994, found: 190.0997.

2,2,6-Trimethylindan-1-one (58) In accordance with the general procedure, a dimethoxyethane solution of 6-methylindan-1-one (1.46 g, 10 mmol), sodium hydride

(80%, 0.90 g, 30 mmol) and methyl iodide (2.0 mL, 30 mmol) was stirred at room temperature for 15 min to give 2,2,6-trimethylindan-1-one (**58**) (1.30 g, 75%); b.p. 94°C (0.2 mm, Kugelrohr); IR (neat) ν 3029, 2969, 2939, 2870, 1726, 1618, 1584, 1494, 1444, 1295, 1284, 1143, 821, 771 cm^{-1}; ^{1}HNMR δ 1.20 (s, 6H), 2.40 (s, 3H), 2.97 (s, 2H), 7.28 (d, J = 8 Hz, 1H), 7.43 (d, J = 8 Hz, 1H), 7.56 (brs, 1H); accurate mass calcd for $C_{12}H_{14}O$: 174.1045, found: 174.1030.

2,2-Dimethyl-5-methoxyindan-1-one (59) By use of the method described in the general procedure, a mixture of 5-methoxyindan-1-one (1.62 g, 10 mmol), methyl iodide (2 mL, 30 mmol) and sodium hydride (80%, 0.90 g, 30 mmol) in dimethoxyethane (35 mL) was stirred for 0.5 h at room temperature to give 2,2-dimethyl-5-methoxyindan-1-one (**59**) (1.80 g, 95%); b.p. 104°C (0.2 mm, Kugelrohr); IR (neat) ν 3068, 3013, 2969, 2933, 2871, 2846, 1712, 1595, 1483, 1438, 1267, 1215, 1067, 1028, 844, 773 cm^{-1}. ^{1}HNMR δ 1.20 (s, 6H), 2.93 (s, 2H), 3.87 (s, 3H), 7.13 (d, J = 8 Hz, 1H), 7.18 (s, 1H), 7.68 (d, J = 8 Hz, 1H); accurate mass calcd for $C_{12}H_{14}O_2$: 190.0994, found: 190.0995.

2,2,5-Trimethylindan-1-one (60) By employing the general procedure, a dimethoxyethane solution (35 mL) of 5-methylindan-1-one (1.46 g, 10 mmol), sodium hydride (80%, 0.90 g, 30 mmol) and methyl iodide (2.0 mL, 30 mmol) was stirred at room temperature for 1.5 h. After workup, the crude product was chromatographed on silica gel and eluted with hexane-ethyl acetate (20:1) to give 2,2,5-trimethylindan-1-one (**60**) (1.50 g, 85 %); b.p. 90°C (0.2 mm, Kugelrohr); IR (neat) ν 3029, 2969, 2939, 2870, 1726, 1618, 1584, 1494, 1444, 1295, 1284, 1143, 821, 771 cm^{-1}; ^{1}HNMR δ 1.20 (s, 6H), 2.40 (s, 3H), 2.93 (s, 2H), 7.13 (d, J = 8 Hz, 1H), 7.20 (s, 1H), 7.63 (d, J = 8 Hz, 1H) ; accurate mass calcd for $C_{12}H_{14}O$: 174.1045, found: 174.1029.

5-Cyano-2,2-dimethylindan-1-one (61) According to the general procedure, a mixture of 5-cyanoindan-1-one (1.57 g, 10 mmol), sodium hydride (80%, 0.90 g, 30 mmol) and methyl iodide (2.0 mL, 30 mmol) was stirred at 0°C for 1 h. After workup, the crude product was recrystallized from ethanol to afford 5-cyano-2,2-dimethylindan-1-one (**61**) (1.60 g, 86%); m.p. 92-93°C; IR (KBr) ν 3047, 2969, 2229, 1712, 1610, 1464, 1435, 1379, 1304, 1276, 1239, 1198, 1108, 995, 931, 838, 770, 743 cm^{-1}; ^{1}HNMR δ 1.23 (s, 6H), 3.07 (s, 2H), 7.68 (d, J = 8 Hz, 1H), 7.76 (s, 1H), 7.85 (d, J = 8 Hz, 1H); ^{13}CNMR δ 25.1, 42.6, 46.0, 117.9, 118.2, 125.2, 130.8, 131.2, 138.6, 152.1, 209.8; m/z 185 (M^+), 170 (base peak); accurate mass calcd for $C_{12}H_{11}NO$: 185.0841, found: 185.0841.

(N-Acetyl-N-methyl-5-amino)-2,2-dimethylindan-1-one (62) Via the general procedure, a mixture of N-acetyl-5-aminoindan-1-one (1.89 g, 10 mmol), sodium hydride (80%, 1.20 g, 40 mmol) and methyl iodide (2.70 mL, 40 mmol) was stirred at -10°C for 30 min. After workup, the mixture was chromatographed on silica gel and eluted with hexane-ethyl acetate (1:1) to give (N-acetyl-N-methyl-5-amino)-2,2-dimethylindan-1-one (**62**) (1.50 g, 65%); b.p. 145°C (0.2 mm, Kugelrohr); IR (neat) ν 2965, 2871, 1709, 1660, 1605, 1485, 1436, 1380, 1350, 1323, 1270, 1201, 1170, 1132, 1107, 1072, 1034, 991, 705 cm^{-1}; ^{1}HNMR δ 1.27 (s, 6H), 1.97 (s, 3H), 3.03 (s, 2H), 3.30 (s, 3H), 7.20 (d, J = 8 Hz, 1H), 7.27 (s, 1H), 7.78 (d, J = 8 Hz, 1H); m/z 231 (M^+), 174 (base peak); accurate mass calcd for $C_{14}H_{17}NO_2$: 231.1259, found: 231.1287.

General procedure for the synthesis of hindered dithioacetal A mixture of ketone (10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) and boron trifluoride etherate (0.5 mL, 3.5 mmol) was heated to 140°C for 2 h. The reaction mixture was cooled to

room temperature, diluted with chloroform and poured into aqueous sodium hydroxide (40 mL, 10%). The organic layer was separated and the aqueous solution was extracted with chloroform. The combined organic solutions were dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo to afford the residue which was then chromatographed on silica gel to give the desired product.

2,2-Dimethyl-1,1-ethylenedithioindane (63) According to the general procedure, a mixture of 2,2-dimethylindan-1-one (1.60 g, 10 mmol), 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was heated to 140°C for 2 h to give 2,2-dimethyl-1,1-ethylenedithioindane (**63**) (1.60 g, 71%) ; b.p. 125°C (0.2 mm, Kugelrohr); IR (neat) ν 3019, 2963, 2924, 2864, 1601, 1465, 1419, 1379, 1276, 744, 435 cm^{-1}; ^{1}HNMR δ 1.21 (s, 6H), 2.78 (s, 2H), 3.24-3.36 (m, 2H), 3.36-3.48(m, 2H), 7.08-7.28 (m, 3H), 7.48 (d, J = 8 Hz, 1H); ^{13}CNMR δ 24.6, 40.2, 46.1, 50.1, 82.6, 124.3, 124.7, 126.9, 127.6, 140.5, 148.3; m/z 236 (M^+), 208 (base peak); anal. calcd. for $C_{13}H_{16}S_2$: C, 66.05, H, 6.82; found C, 65.99, H, 6.92.

2,2-Dimethyl-1,1-ethylenedithiotetralin (64) By use of the method described in the general procedure, a mixture of 2,2-dimethyltetra-1-one (1.74 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was heated to 140°C for 2 h to give 2,2-dimethyl-1,1-ethylenedithiotetraline (64) (1.90 g, 77%); m.p. 76-77°C; IR (KBr) ν 3020, 2855, 1933, 1600, 1427, 1378, 1354, 1278, 1240, 1154, 1101, 1016, 946, 899, 845, 762, 728 cm^{-1}; ^{1}HNMR δ 1.20 (s, 6H), 1.93 (t, J = 6 Hz, 2H), 2.83 (t, J = 6 Hz, 2H), 3.32-3.44 (m, 2H), 3.44-3.56 (m, 2H), 6.98 (d, J = 8 Hz, 1H), 7.06-7.22 (m, 2H), 7.92 (d, J = 8 Hz, 1H); ^{13}CNMR δ 25.4, 26.0, 35.9, 40.0, 42.5, 80.0, 126.0, 126.5, 128.4, 130.3, 134.5, 142.7; m/z 250 (M^+), 166 (base peak); anal. calcd. for $C_{14}H_{18}S_2$: C, 67.15, H, 7.19; found C, 67.12, H, 7.19.

2,2-Dimethyl-6-methoxy-1,1-ethylenedithioindane (65) In accordance with the general procedure, a mixture of 6-methoxy-2,2-dimethylindan-1-one (1.90 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) and boron trifluoride etherate (0.5 mL) was heated to 140°C for 2 h to yield 2,2-dimethyl-6-methoxy-1,1-ethylenedithioindane (**65**) (2.60 g, 98%); b.p. 144°C (0.2 mm, Kugelrohr); IR (neat) ν 3080, 2960, 1606, 1450, 1398, 1370, 1320, 1270, 1240, 1182, 1150, 1090, 1034, 850, 800, 750 cm^{-1}; ^{1}HNMR δ 1.23 (s, 6H), 2.77 (s, 2H), 3.24-3.36 (m, 2H), 3.26-3.48 (m, 2H), 3.87 (s, 3H), 6.72 (dd, J = 2, 8 Hz, 1H), 7.02 (d, J = 8 Hz, 1H), 7.04 (s, 1H); ^{13}CNMR δ 24.6, 40.2, 45.3, 50.6, 55.5, 82.8, 108.8, 114.0, 125.3, 132.6, 149.7, 159.3; m/z 266 (M^+), 238 (base peak); anal calcd for $C_{14}H_{18}OS_2$: C, 63.12, H, 6.81; found C, 63.12, H, 6.96.

2,2,6-Trimethyl-1,1-ethylenedithioindane (66) By use of the general procedure, a mixture of 2,2,6-trimethylindan-1-one (1.74 g, 10 mmol) and 1,2-ethanedithiol (2.80 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was treated at 140°C for 2 h to yield 2,2,6-trimethyl-1,1-ethylenedithioindane (**66**) (1.65 g, 66%); b.p. 135°C (0.2 mm, Kugelrohr); IR (neat) ν 3017, 2962, 2922, 2863, 2837, 1488, 1455, 1378, 1359, 1276, 794 cm^{-1}; ^{1}HNMR δ 1.24 (s, 6H), 2.35 (s, 3H), 2.76 (s, 2H), 3.24-3.36 (m, 2H), 3.36-3.48 (m, 2H), 6.98 (d, J = 8 Hz, 1H), 7.02 (d, J = 8 Hz, 1H), 7.30 (brs, 1H); ^{13}CNMR δ 21.4, 24.6, 40.3, 45.7, 50.3, 82.6, 124.4, 124.8, 128.6, 136.5, 137.6, 148.2; m/z 250 (M^+), 222 (base peak); anal. calcd. for $C_{14}H_{18}S_2$: C, 67.15, H, 7.19; found C, 66.95, H, 7.25.

2,2-Dimethyl-5-methoxy-1,1-ethylenedithioindane (67) A mixture of 2,2-dimethyl-5-methoxyindan-1-one (1.90 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was allowed to react for 2 h according to the general procedure described above. After workup, the mixture was chromatographed

on silica gel and eluted with hexane-ethyl acetate (10:1) to give 2,2-dimethyl-5-methoxy-1,1-ethylenedithioindane (**67**) (2.20 g, 83%); m.p. 49-50°C; IR (KBr) ν 3005, 2930, 1588, 1482, 1441, 1376, 1358, 1313, 1270, 1142, 1109, 1085, 1026, 842, 789, 709 cm^{-1}; ^{1}HNMR δ 1.20 (s, 6H), 2.73 (s, 2H), 3.22-3.34 (m, 2H), 3.34-3.48 (m, 2H), 3.80 (s, 3H), 6.68 (s, 1H), 6.76 (d, J = 8 Hz, 1H), 7.40 (d, J = 8 Hz, 1H); ^{13}CNMR δ 24.7, 40.2, 46.3, 50.5, 55.5, 82.3, 110.1, 112.9, 125.2, 140.3, 142.1, 159.8; m/z 266 (M^+), 238 (base peak); anal calcd for $C_{14}H_{18}OS_2$: C, 63.12, H, 6.81; found C, 63.02, H, 6.96.

2,2,5-Trimethyl-1,1-ethylenedithioindane (68) According to the general procedure, a mixture of 2,2,5-trimethylindan-1-one (1.74 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was heated to 140°C for 2 h. After workup, the crude product was distilled to give 2,2,5-trimethyl-1,1-ethylenedithioindane (**68**) (2.15 g, 86%); b.p. 132°C (0.2 mm, Kugelrohr); IR (neat) ν 3005, 2963, 2922, 2863, 2837, 1464, 1359, 1275, 814, 789 cm^{-1}; ^{1}HNMR δ 1.24 (s, 6H), 2.32 (s, 3H), 2.76 (s, 2H), 3.24-3.36 (m, 2H), 3.36-3.48 (m, 2H), 6.96 (s, 1H), 7.02 (d, J = 8 Hz, 1H), 7.36 (d, J = 8 Hz, 1H); ^{13}CNMR δ 21.3, 24.7, 40.2, 46.0, 50.2, 82.0, 124.1, 125.3, 127.7, 137.4, 140.6, 145.5; m/z 250 (M^+), 222 (base peak); anal. calcd. for $C_{14}H_{18}S_2$: C, 67.15, H, 7.19; found C, 66.78, H, 7.31.

5-Cyano-2,2-dimethyl-1,1-ethylenedithioindane (69) According to the general procedure, a mixture of 5-cyano-2,2-dimethylindan-1-one (1.85 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate was treated at 140°C for 2 h to give the crude product which was recrystallized from ethanol to afford 5-cyano-2,2-dimethyl-1,1-ethylenedithioindane (**69**) (2.30 g, 92%); m.p. 93-95°C; IR (KBr) ν 3000,

2961, 2226, 1605, 1463, 1381, 1364, 1294, 1278, 1245, 1183, 1105, 974, 927, 878, 866, 791, 739, 712 cm^{-1}; ^{1}HNMR δ 1.21 (s, 6H) , 2.80 (s, 2H), 3.28-3.47 (m, 4H), 7.42 (s, 1H), 7.51 (d, J = 8 Hz, 1H), 7.57 (d, J = 8 Hz, 1H); ^{13}CNMR δ 24.2, 20.4, 45.4, 50, 81.7, 111.1, 119.1, 125.0, 128.3, 131.2, 141.5, 154.0; m/z 261 (M^+), 233 (base peak); anal. calcd. for $C_{14}H_{15}NS_2$: C, 64.33, H, 5.78, N, 5.36, found C, 64.22, H, 5.39, N, 5.18.

(N-Acetyl-N-methyl-5-amino)-2,2-dimethyl-1,1-ethylenedithioindane (70) By employing the general procedure, a mixture of (N-acetyl-N-methyl-5-amino)-2,2-dimethylindan-1-one (2.31 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate was treated at 140°C for 2 h to give the crude product which was recrystallized from hexane-ethyl acetate (1: 1) to afford (N-acetyl-N-methyl-5-amino)-2,2-dimethyl-1,1-ethylenedithioindane (**70**) (2.60 g, 85%); m.p. 172-173°C; IR (KBr) ν 3035, 2958, 1653, 1607, 1482, 1422, 1374, 1348, 1313, 1279, 1164, 1130, 1069, 976, 878, 730, 602 cm^{-1}; ^{1}HNMR δ 1.23 (s, 6H), 1.87 (s, 3H), 2.80 (s, 2H), 3.23 (s, 3H), 3.24-3.40 (m, 2H), 3.40-3.52 (m, 2H), 6.96 (s, 1H), 7.04 (d, J = 8 Hz, 1H), 7.52 (d, J = 8 Hz, 1H); ^{13}CNMR δ 22.4, 24.5, 37.2, 40.4, 45.8, 50.4, 81.8, 123.3, 125.4, 125.8, 142.2, 144.0, 147.9, 170.6; accurate mass calcd for $C_{16}H_{21}NOS_2$: 307.1064, found: 307.1058; anal. calcd.: C, 62.50, H, 6.88; found C, 62.84, H, 7.06.

4-Bromo-2,2-dimethyltetra-1-one (71) A mixture of 2,2-dimethyltetra-1-one (1.80 g, 0.01 mol), N-bromosuccimide (1.80 g, 0.01 mol) and AIBN (0.1 g) was dissolved in carbon tetrachloride (30 mL). The solution was irradiated with a sun lamp and heated under reflux for 3 h . After being cooled to room temperature and then filtered, the filtrate was washed with sodium thiosulfate (20%, 50 mL), water (50 mL), dried over anhydrous magnesium sulfate and evaporated in vacuo to give the oil which was then chromatographed on silica gel and eluted with hexane-ethyl acetate (15:1) to yield 4-bromo-

2,2-dimethyltetra-1-one (**71**) (2.00 g, 79%); IR (neat) ν 3070, 3033, 2934, 1699, 1603, 1472, 1455, 1385, 1330, 1300, 1202, 1184, 1160, 1125, 1097, 1012, 992, 969, 947, 808, 795, 741 cm^{-1}; ^{1}HNMR δ 1.23 (s, 3H), 1.33 (s, 3H), 2.70 (d, J = 8 Hz, 2H), 5.80 (t, J = 8 Hz, 1H), 7.07-7.77 (m, 3H), 8.03 (dd, J = 2, 8 Hz, 1H); m/z 253 (M^+), 173 (base peak).

1,2-dihydro-2,2-dimethylnapthalen-1-one (72) A mixture of 4-bromo-2,2-dimethyltetra-1-one (1.50 g, 6 mmol) and potassium t-butoxide (2.00 g, 18 mmol) in t-butanol (25 mL) was refluxed for 1 h. The mixture was poured into water (30 mL) and was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo to afford the residue which was purified by chromatography on silica gel and eluted with hexane-ethyl acetate (15:1) to yield 1,2-dihydro-2,2-dimethylnapthalen-1-one (**72**) (1.00 g, 99%); b.p. 86°C (0.2 mm); IR (neat) ν 3064, 3032, 2968, 2929, 1671, 1646, 1599, 1469, 1453, 1370, 1306, 1235, 1217, 1191, 989, 969, 880, 791, 718 cm^{-1}; ^{1}HNMR δ 1.20 (s, 6H), 6.32 (d, J = 10 Hz, 1H), 6.58 (d, J =10 Hz, 1H), 7.70-7.77 (m, 3H), 8.05 (dd, J = 2, 8 Hz, 1H); accurate mass calcd for $C_{12}H_{12}O$: 172.0888, found: 172.0878

1,2-dihydro-2,2-dimethylnapthalen-1-thione (73) A mixture of 1,2-dihydro-2,2-dimethylnapthalen-1-one (0.50 g, 2.91 mmol) and phosphorous pentasulfide (0.20 g, 0.90 mmol) in pyridine (25 mL) was heated to 90°C overnight. The reaction mixture was poured into hydrochloric acid (10%, 40%) and was extracted with hexane. The combined organic solution were washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo to give the blue oil which was then chromatographed on silica gel and eluted with hexane to afford 1,2-dihydro-2,2-dimethylnapthalen-1-thione (**73**) as blue [illegible] (0.5 g, 91%); b.p. 96°C (0.2 mm,

Kugelrohr); IR (neat) ν 3067, 3038, 2973, 2871, 1677, 1647, 1602, 1578, 1478, 1466, 1315, 1289, 1256, 1159, 1097, 910, 792, 734 cm^{-1}; ^{1}HNMR δ 1.20 (s, 6H), 6.32 (d, J = 10 Hz, 1H), 6.58 (d, J =10 Hz, 1H), 7.00-7.73 (m, 3H), 8.40 (dd, J = 1, 8 Hz, 1H); ^{13}CNMR δ 32.0, 54.1, 123.3, 126.5, 127.3, 127.9, 129.8, 132.0, 134.0, 144.6, 247.6; accurate mass calcd for $C_{12}H_{12}S$: 188.0660, found: 188.0639.

General procedure for the reaction between dithioacetal with tungsten hexacarbonyl Dithioacetal (1.00 mmol) and tungsten hexacarbonyl (530 mg, 1.50 mmol) were dissolved in chlorobenzene (5 mL). The solution was heated to 160°C under nitrogen atmosphere for 8-24 h. After being cooled to room temperature, chlorobenzene was removed by vacuum distillation. The blackish residue was then taken up in chloroform. After filtration, the filtrate was evaporated in vacuo and the residue was chromatographed on silica gel and the product(s) was (were) subjected to spectroscopic and/or elementary analysis.

Desulfurdimerization of 2,2-dimethyl-1,1-ethylenedithioindane (63) According to the general procedure, a mixture of 2,2-dimethyl-1,1-ethylenedithioindane (236 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was treated for 18 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane to yield 2,3-dimethylindene[59] (**74**) (14.1 mg, 10%); ^{1}HNMR δ 2.03 (s, 6H), 3.27 (s, 2H), 6.90-7.55 (m, 4H); E-1-(2,2-dimethyl-1-indanyliden)-2,2-dimethylindane (**75**) (44.4 mg, 31%); m.p. 127-129°C (lit.[60] m.p. 129-130°C) ; m/z 288 (M^+), 271 (base peak); ^{1}HNMR δ 1.33 (s, 12H), 2.80 (s, 4H), 7.12-7.24 (m, 6H), 7.48-7.56 (d, J = 8 Hz, 2H); ^{13}CNMR δ 27.7, 50.7, 52.3, 124.2, 124.9, 127.2, 128.0, 143.0, 145.3, 146.1; anal. calcd. for $C_{22}H_{24}$: C, 91.96, H, 8.39; found C, 91.51, H, 8.42; 2,2-dimethylindan-1-thione (**76**) (52.8 mg, 30%); b.p. 80°C (0.2 mm, Kugelrohr); IR (neat) ν 3070, 2963, 2864, 1601, 1578, 1464, 1433, 1378, 1322, 1291, 1265, 1150,

1119, 1101, 1078, 1016, 971, 770, 715 cm^{-1}; ^{1}HNMR δ 1.33 (s, 6H), 3.13 (s, 2H), 7.36 (t, J = 8 Hz, 1H), 7.48 (d, J = 8 Hz, 1H), 7.64 (t, J = 8 Hz, 1H), 7.94 (d, J = 8 Hz, 1H); ^{13}CNMR δ 29.7, 46.8, 56.8, 125.2, 126.2, 127.7, 134.7, 145.4, 152.2, 254.7; anal. calcd. for $C_{11}H_{12}S$: C, 74.95, H, 6.86; found C, 74.18, H, 6.70.

2,2-Dimethylindan-1-thiol (77) Under nitrogen atmosphere, a solution of 2,2-dimethylindan-1-thione (**76**) (3.50 g, 0.02 mol) in THF (5 mL) was added dropwise to a slurry containing lithium aluminum hydride (0.8 g, 0.021 mol) in THF (20 mL). The mixture was stirred for 0.5 h, water (30 mL) was added and the mixture was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo. The crude product was distilled to yield 2,2-dimethylindan-1-thiol (**77**) (3.40 g, 96%); b.p. 74°C (0.2 mm, Kugelrohr); IR (neat) ν 3073, 3028, 2901, 2843, 1956, 1609, 1589, 1467, 1384, 1366, 1297, 1266, 1234, 1208, 1764, 1107, 1022, 940, 929, 760, 735 cm^{-1}; ^{1}HNMR δ 1.03 (s, 3H), 1.20 (s, 3H), 1.47 (d, J = 8 Hz, 1H), 2.73 (br, 2H), 4.00 (d, J = 8 Hz, 1H), 7.07-7.43 (m, 4H); ^{13}CNMR δ 23.6, 26.9, 44.9, 45.9, 54.4, 124.5, 124.7, 126.6, 127.2, 141.6, 145.4; m/z 178 (M^+), 145 (base peak).

Desulfurdimerization of 2,2-dimethyl-1,1-ethylenedithiotetraline (64) Via the general procedure, a mixture of 2,2-dimethyl-1,1-ethylenedithiotetraline (250 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed for 24 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane-ethyl acetate (20:1) which gave E-1-(2,2-dimethyltetrayliden)-2,2-dimethyltetralin (**78**) (23.7 mg, 15%); m.p. 194-196°C (lit.[61] m.p. 195°C); ^{1}HNMR δ 0.64 (s, 6H), 1.06 (s, 6H), 1.53-2.80 (m, 8H), 7.00-7.20 (m, 8H); 2,2-dimethyltetra-1-thione (**79**) (15.8 mg, 9%); ^{1}HNMR δ 1.37 (s, 6H), 1.97 (t, J = 6 Hz, 2H), 3.00 (t, J = 6 Hz, 2H), 6.18 (t, J = 8 Hz, 1H), 7.26 (d, J = 8 Hz, 1H), 7.47 (t, J = 8 Hz, 1H), 8.35

(d, J = 8 Hz, 1H); ^{13}CNMR δ 26.5, 29.6, 36.7, 49.5, 126.6, 128.9, 130.7, 132.8, 137.0, 139.3, 250.0; accurate mass calcd for $C_{12}H_{14}S$: 190.0816, found: 190.0822.

Reaction of 2,2-dimethyl-6-methoxy-1,1-ethylenedithioindane (65) with tungsten hexacarbonyl By employing the general procedure, a mixture of 2,2-dimethyl-6-methoxy-1,1-ethylenedithioindane (266 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed for 24 h. After usual workup, the mixture was chromatographed on silica gel and eluted with hexane to give 2,2-dimethyl-6-methoxyindan-1-thione (**80**) (53.9 mg, 26%); b.p. 116°C (0.2 mm, Kugelrohr); IR (neat) ν 3057, 3006, 2963, 2927, 1610, 1577, 1486, 1464, 1429, 1379, 1357, 1336, 1313, 1282, 1170, 1026, 985, 862, 819, 761 cm^{-1}; ^{1}HNMR δ 1.38 (s, 6H), 3.04 (s, 2H), 3.83 (s, 3H), 7.23 (dd, J = 3, 8 Hz, 1H), 7.33 (d, J = 8 Hz, 1H), 7.36 (d, J = 3 Hz, 1H); ^{13}CNMR δ 29.8, 46.3, 55.7, 57.5, 106.5, 124.5, 127.0, 145.4, 146.5, 160.0, 254.3; accurate mass calcd for $C_{12}H_{14}OS$: 206.0765, found: 206.0762.

Reaction of 2,2,6-trimethyl-1,1-ethylenedithioindane (66) with tungsten hexacarbonyl According to the general procedure, a mixture of 2,2,6-trimethyl-1,1-ethylenedithioindane (250 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene was allowed to react for 18 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane to afford 2,2,6-trimethylindan-1-thione (**81**) (79.8 mg, 42%) as purple oil; b.p. 96°C (0.2 mm, Kugelrohr); IR (neat) ν 3029, 2964, 2924, 2865, 1614, 1574, 1487, 1464, 1437, 1419, 1380, 1357, 1413, 1279, 1265, 1224, 1190, 1167, 1097, 1074, 1033, 973, 893, 812, 756 cm^{-1}; ^{1}HNMR δ 1.33 (s, 6H), 2.40 (s, 3H), 3.07 (s, 2H), 7.32 (d, J = 8 Hz, 1H), 7.43 (d, J = 8 Hz, 1H), 7.75 (s, 1H); ^{13}CNMR δ 20.9, 29.7, 46.4, 56.9, 125.0, 125.8, 136.1, 137.6, 145.4, 149.5, 254.5; accurate mass calcd for $C_{12}H_{14}S$: 190.0816, found: 190.0825.

Reaction of 2,2-dimethyl-5-methoxy-1,1-ethylenedithioindane (67) with tungsten hexacarbonyl By use of the general procedure, 2,2-dimethyl-5-methoxy-1,1-ethylenedithioindane (266 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed for 8 h. After workup, the mixture was chromatographed on silica gel and eluted which hexane-ethyl-acetate (10:1) to afford 2,2-dimethyl-5-methoxyindan-1-thione (**82**) (74.8 mg, 36%) as purple oil; b.p. 110°C (0.2 mm, Kugelrohr); IR (neat) ν 3050, 2926, 2840, 1605, 1485, 1443, 1322, 1264, 1249, 1197, 1176, 1139, 1078, 1024, 881, 867, 825, 761, 736 cm^{-1}; ^{1}HNMR δ 1.32 (s, 6H), 3.05 (s, 2H), 3.87 (s, 3H), 6.83-6.87 (m, 2H), 7.87 (d, J = 9 Hz, 1H); ^{13}CNMR δ 29.6, 48.8, 55.7, 56.3, 108.8, 116.0, 127.1, 139.8, 155.3, 166.0, 250.6; accurate mass calcd for $C_{12}H_{14}OS$: 206.0765, found: 206.0768.

Reaction of 2,2,5-trimethyl-1,1-ethylenedithioindane (68) with tungsten hexacarbonyl A solution of 2,2,5-trimethyl-1,1-ethylenedithioindane (250 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was treated according to the general procedure for 8 h. After work up, the mixture was chromatographed on silica gel and eluted which hexane to yield 2,2,5-trimethylindan-1-thione (**83**) (72.2 mg, 38%) as red oil; b.p. 100°C (0.2 mm, Kugelrohr); IR (neat) ν 3040, 2962, 2864, 1607, 1576, 1465, 1434, 1379, 1358, 1312, 1292, 1264, 1248, 1177, 1129, 1085, 1034, 973, 932, 822, 743 cm^{-1}; ^{1}HNMR δ 1.33 (s, 6H), 2.37 (s, 3H), 3.04 (s, 2H), 7.14 (d, J = 8 Hz, 1H), 7.23 (s, 1H), 7.84 (d, J = 8 Hz, 1H); ^{13}CNMR δ 22.1, 29.7, 46.6, 56.6, 125.1, 126.4, 128.7, 129.1, 146.2, 152.5, 254.9; accurate mass calcd for $C_{12}H_{14}S$: 190.0816, found: 190.0812.

Attempted desulfurization of 5-cyano-2,2-dimethyl-1,1-ethylenedithioindane (69) A mixture of 5-cyano-2,2-dimethyl-1,1-ethylenedithioindane (261 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50

mmol) in chlorobenzene (5.0 mL) was treated for 72 h according to the general procedure. Workup gave starting material (**69**) (251 mg, 96%) which showed the same physical properties with **69**.

Attempted desulfurization of (N-acetyl-N-methyl-5-amino)-2,2-dimethyl-1,1-ethylenedithioindane (70) Via the general procedure, a mixture of (N-acetyl-N-methyl-5-amino)-2,2-dimethyl-1,1-ethylenedithioindane (307 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed for 72 h. Workup gave starting material (**70**) (289 mg, 94%) which showed the same physical properties with **70**.

Reaction of 2,2-diphenyl-1,3-oxthiolane with tungsten hexacarbonyl According to the general procedure, a mixture of 2,2-diphenyl-1,3-oxthiolane (**84**) (242 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed 24 h. After workup, the crude product was chromatographed on silica gel and eluted with hexane-ethyl acetate (10:1) to afford benzophenone (**85**) (180 mg, 99%) which show same physical properties as those of the authentic sample.

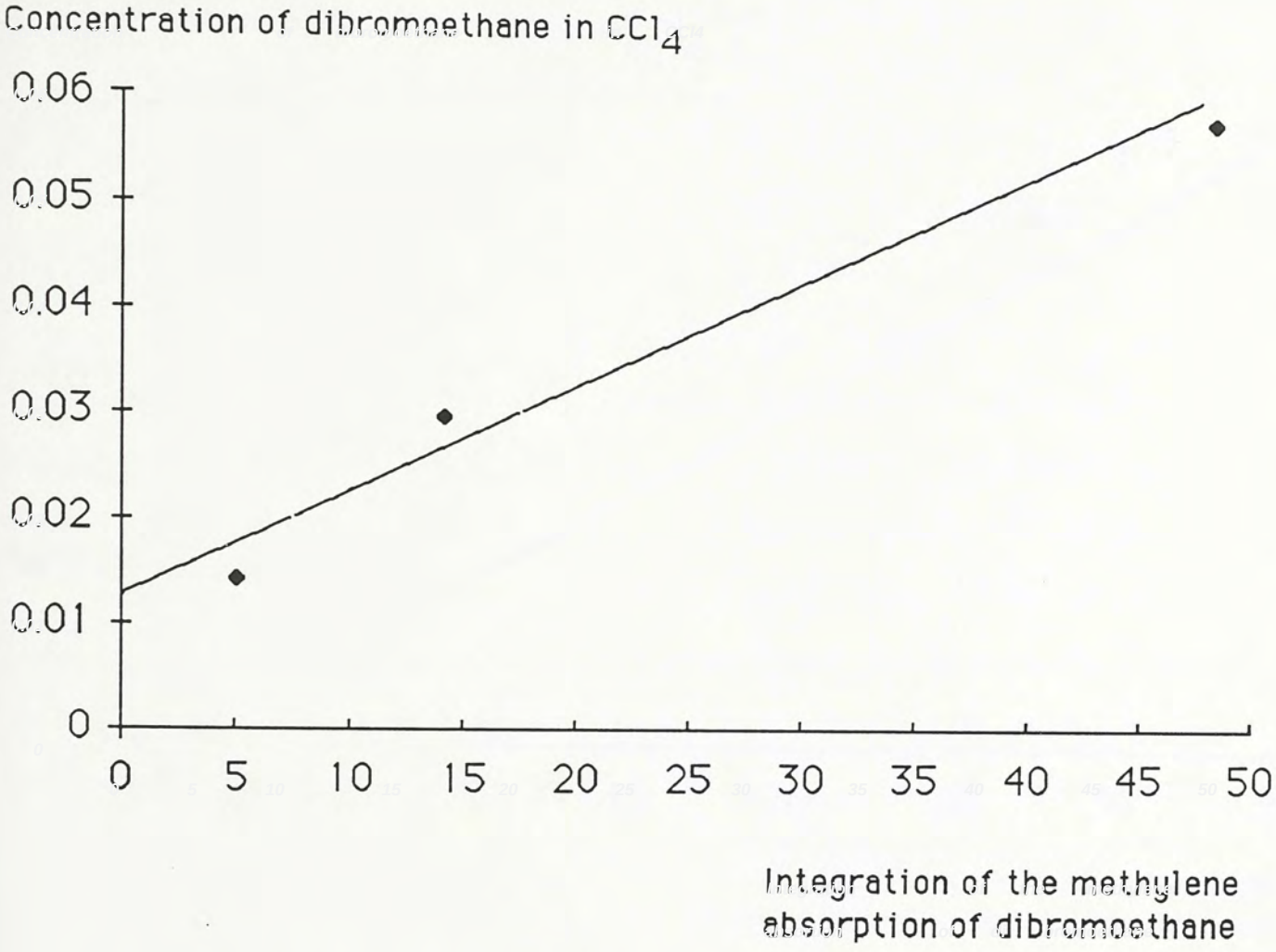
Ethene determination from the reaction of 2,2-dimethyl-1,1-ethylenedithioindane with tungsten hexacarbonyl A mixture of 2,2-dimethyl-1,1-ethylenedithioindane (760.1 mg, 3.22 mmol) and tungsten hexacarbonyl (1700 mg, 4.83 mmol) in chlorobenzene (15 mL) was flushed with nitrogen and then heated to 160°C for 24 h. The outlet of the reaction flask was connected to a tube which was dipped into a tetrachloromethane (100 mL) solution containing bromine (1 mL). The blackish mixture was cooled to room temperature and the tetrachloromethane solution was washed with sodium thiosulfate (20%, 100 mL), dried over anhydrous magnesium sulfate, filtered and the filtrate was diluted to 100 mL in a volumetric flask. Three dibromoethane solutions in

tetrachloromethane with different concentrations (0.0144M, 0.0298M and 0.0577M) were prepared for calibrating the concentration of dibromoethane (Figure 10). By comparing integration of the methylene absorption of dibromoethane in NMR, the yield of dibromoethane (92%) was obtained; ^{1}HNMR δ : 3.71 (s, 4H).

Ethene determination from the reaction of 2,2-diphenyl-1,3-oxthiolane with tungsten hexacarbonyl According to the procedure describe above, a mixture of 2,2-diphenyl-1,3-oxthiolane (972.4 mg, 4.00 mmol) and tungsten hexacarbonyl (1400 mg, 4.00 mmol) in chlorobenzene (20 mL) was refluxed for 24 h. The outlet of the reaction flask was connected to a tube which dipped into tetrachloromethane (100 mL) containing bromine (1 mL). After workup, the tetrachloromethane solution was diluted to 100 mL in a volumetric flask. Three dibromoethane solutions in tetrachloromethane with different concentrations (0.0210 M, 0.0369 M, 0.0623 M) were prepared for calibrating the concentration of dibromoethane in the reaction (Figure 11). By comparing integration of the methylene absorption of dibromoethane in NMR, the yield of dibromoethane (62%) was obtained; ^{1}HNMR δ : 3.71 (s, 4H).

2,2-Dimethylindan-1-yl 2-bromoethyl sulfide (86) A solution of 2,2-dimethylindan-1-thiol (1.00 g, 5.70 mmol) in dimethoxyethane (10 mL) was added dropwise to a slurry containing sodium hydride (80%, 0.30 g, 10 mmol) in dimethoxyethane (20 mL) under nitrogen atmosphere. The mixture was stirred for 10 min and was syringed to dibromoethane (5 mL) in dimethoxyethane (10 mL) over a period of 15 min. After stirring for 30 min, water (40 mL) was added and the mixture was extracted with ether. The combined organic solution were washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo. Dibromoethane was removed by vacuum distillation to give the residue which was chromatographed on silica gel and eluted with hexane-ethyl ac (10:1 ield 2,2-dimethylindan-1-yl) 2-

Figure 5: Calibration curve of the concentration of dibromoethane for the reaction of **63** with tungsten hexacarbonyl

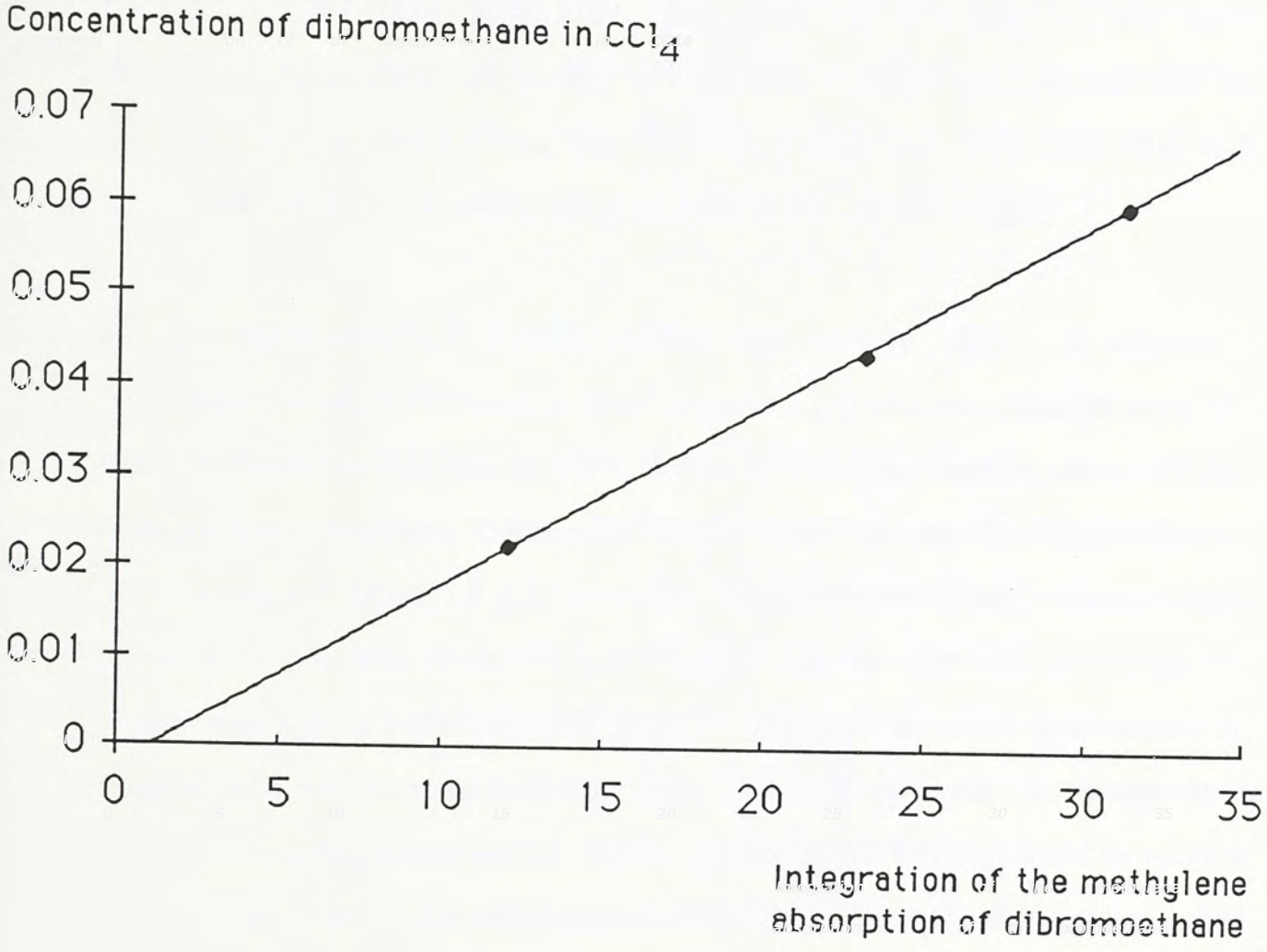


y-intercept = 1.26×10^{-2}

slope = 9.55×10^{-4}

$r = 0.975$

Figure6 : Calibration curve of the concentration of dibromoethane for the reaction of **84** with tungsten hexacarbonyl



y-intercept = -5.10×10^{-4}

slope = 1.97×10^{-3}

$r = 0.999$

bromoethyl sulfide (**86**) (1.00 g, 69%); IR (neat) ν 3073, 3027, 2961, 2869, 1608, 1437, 1383, 1365, 1299, 1256, 1231, 1189, 1106, 1022, 938, 899, 792, 732, 609 cm^{-1}; ^{1}HNMR δ 1.10 (s, 3H), 1.20 (s, 3H), 2.77 (m, 2H), 2.80-3.17 (m, 2H), 3.27-3.63 (m, 2H), 3.83 (s, 1H), 7.07-7.47 (m, 4H); ^{13}CNMR δ 24.1, 28.0, 30.4, 34.6, 45.4, 46.3, 61.5, 124.9, 126.4, 127.5, 142.1, 143.5; m/z 285 (M^+), 257 (base peak).

2,2-dimethylindan-1-yl 2-thiophenoxyethyl sulfide (87) A solution of thiophenol (1.0 mL, 9.10 mmol) in dimethoxyethane (10 mL) was added dropwise to a slurry containing sodium hydride (80%, 0.30 g, 10 mmol) in dimethoxyethane (20 mL) under nitrogen atmosphere. The mixture was stirred for 5 min and (2,2-dimethylindan-1-yl)-2'-bromoethyl sulfide (1.0 g, 3.50 mmol) in dimethoxyethane (5 mL) was added over a period of 15 min. After stirring for 1 h, water (40 mL) was added and the mixture was washed with sodium hydroxide (10%, 50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the filtrate was evaporated in vacuo to give the residue which was chromatographed on silica gel and eluted with hexane-ethyl acetate (1:10) to yield 2,2-dimethylindan-1-yl 2-thiophenoxyethyl sulfide (**87**) (1.00 g, 91%); b.p. 170°C (0.2 mm, Kugelrohr); IR (neat) ν 3069, 3020, 2956, 2927, 2864, 1585, 1477, 1461, 1439, 1363, 1196, 1025, 736, 690 cm^{-1}; ^{1}HNMR δ 1.10 (s, 3H), 1.17 (s, 3H), 2.53-2.90 (m, 2H), 2.70 (m, 2H), 2.93-3.27 (m, 2H), 3.80 (s, 1H), 7.03-7.50 (m, 9H); ^{13}CNMR δ 24.3, 28.2, 32.1, 34.8, 45.4, 46.5, 61.4, 124.9, 125.1, 126.5, 126.6, 127.4, 129.1, 130.3, 135.7, 142.3, 143.9; accurate mass calcd for $C_{19}H_{22}S_2$: 314.1163, found: 314.1161.

Preparation of 2,2-dimethylindan-1-yl vinyl sulfide (88) A mixture of 2,2-dimethylindan-1-yl 2-bromoethyl sulfide (103 mg, 0.36 mmol) and t-butoxide (120 mg, 1.08 mmol) in t-butanol (5 mL) was refluxed for 24 h. The mixture was poured into water

(10 mL) and was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate was evaporated in vacuo to afford the residue which was purified by chromatography on silica gel and eluted with hexane-ethyl acetate (20:1) to yield 2,2-dimethylindan-1-yl vinyl sulfide (**88**) (45.3 mg, 62%); ^{1}HNMR δ 1.09 (s, 3H), 1.25 (s, 3H), 2.74 (s, 2H), 4.09 (s, 1H), 5.14 (d, J = 10 Hz, 1H), 5.26 (d, J = 16 Hz, 1H), 6.38 (dd, J = 10, 16 Hz, 1H), 7.03-7.46 (m, 4H); which decomposed in chloroform solution.

Reaction of t-butyl adamantane-1-peroxycarboxylate[40] with 2,2-dimethylindan-1-yl) 2-thiophenoxyethyl sulfide Under nitrogen atmosphere, a mixture of 2,2-dimethylindan-1-yl 2-thiophenoxyethyl sulfide (**87**) (326 mg, 1.04 mmol) and t-butyl adamantane-1-peroxycarboxylate (**89**) (252 mg, 1.00 mmol) in chlorobenzene (5 mL) was refluxed for 24 h . After being cooled to room temperature, chlorobenzene was removed by vacuum distillation. The residue was then chromatographed on silica gel and eluted with hexane-ethyl acetate (10:1) to give 2,2-dimethylindan-1-one (**55**) (65.6 mg, 42%) and brown oil which was further chromatographed on silica gel and eluted with n-hexane to yield diphenyl disulfide (**90**) (74.1 mg, 34%); m.p. 53-55°C (lit.[62] 58-60°C), (2,2-dimethylindan-1-yl)-vinyl sulfide (**88**) (16.3 mg, 8%) which exhibited same physical properties as the sample prepared independently from above; phenyl vinyl sulfide[63] (**91**) (4.1 mg, 3%); ^{1}HNMR δ 5.34 (d, J = 16 Hz, 1H), 5.35 (d, J = 10 Hz, 1H), 6.54 (dd, J = 10, 16 Hz, 1H), 6.90-7.50 (m, 5H), 2,2-dimethylindan-1-thione (**76**) (trace) and (2,2-dimethylindan-1-yl)-2'-thiophenoethyl sulfide (**87**) (115 mg, 35%) which also exhibited same physical properties as those of the authentic samples.

Reaction of t-butyl adamantane-1-peroxycarboxylate with 2,2-dimethylindan-1-thione (76) A mixture of 2,2-dimethylindan-1-thione (**76**) (210 mg, 1.17 mmol) and t-butyl adamantane-1-peroxycarboxylate (**89**) (295 mg, 1.17 mmol)

in chlorobenzene (5 mL) was refluxed for 24 h under nitrogen atmosphere. After being cooled to room temperature, chlorobenzene was removed by vacuum distillation. The residue was then chromatographed on silica gel and eluted with hexane-ethyl acetate (10:1) to afford 2,2-dimethylindan-1-thione (**76**) (70 mg, 33%) and 2,2-dimethylindan-1-one (**55**) (121 mg, 65%) which exhibited same physical properties as those of the authentic samples.

Desulfurdimerization of 2,2-dimethylindan-1-thione (76) with tungsten hexacarbonyl Via the same procedure as described above, a mixture of 2,2-dimethylindan-1-thione (300 mg, 1.70 mmol) and tungsten hexacarbonyl (897 mg, 2.55 mmol) in chlorobenzene (5.0 mL) was treated for 24 h. After workup, the residue was chromatographed on silica gel and eluted with hexane to give E-1-(2,2-dimethyl-1-indanyliden)-2,2-dimethylindane (**75**) (60 mg, 24%) and 2,2-dimethylindan-1-thione (**76**) (195 mg, 65%) which exhibited same physical properties as those of the authentic sample. In a separate run, a mixture of 2,2-dimethylindan-1-thione (264 mg, 1.50 mmol) and tungsten hexacarbonyl (792 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was treated for 72 h via the same procedure as described above After workup, the residue was chromatographed on silica gel and eluted with hexane to give 2,3-dimethylindene (**74**) (74.3 mg, 34%) and E-1-(2,2-dimethyl-1-indanyliden)-2,2-dimethylindane (**75**) (41.0 mg, 19%). Both compounds exhibited same physical properties as those of the authentic samples.

Desulfurization of 1,2-dihydro-2,2-dimethylnaptha-1-thione (73) with tungsten hexacarbonyl A chlorobenzene solution (5 mL) of 1,2-dihydro-2,2-dimethylnaptha-1-thione (190 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) was allowed to react for 24 h according to the general procedure. After workup, the residue was chromatographed on silica gel and eluted with hexane to afford 1,2-

dimethylnapthalene[64] (**92**) (70.2 mg, 45%); ^{1}HNMR δ 2.47 (s, 3H), 2.57 (s, 3H), 7.07-8.07 (m, 6H).

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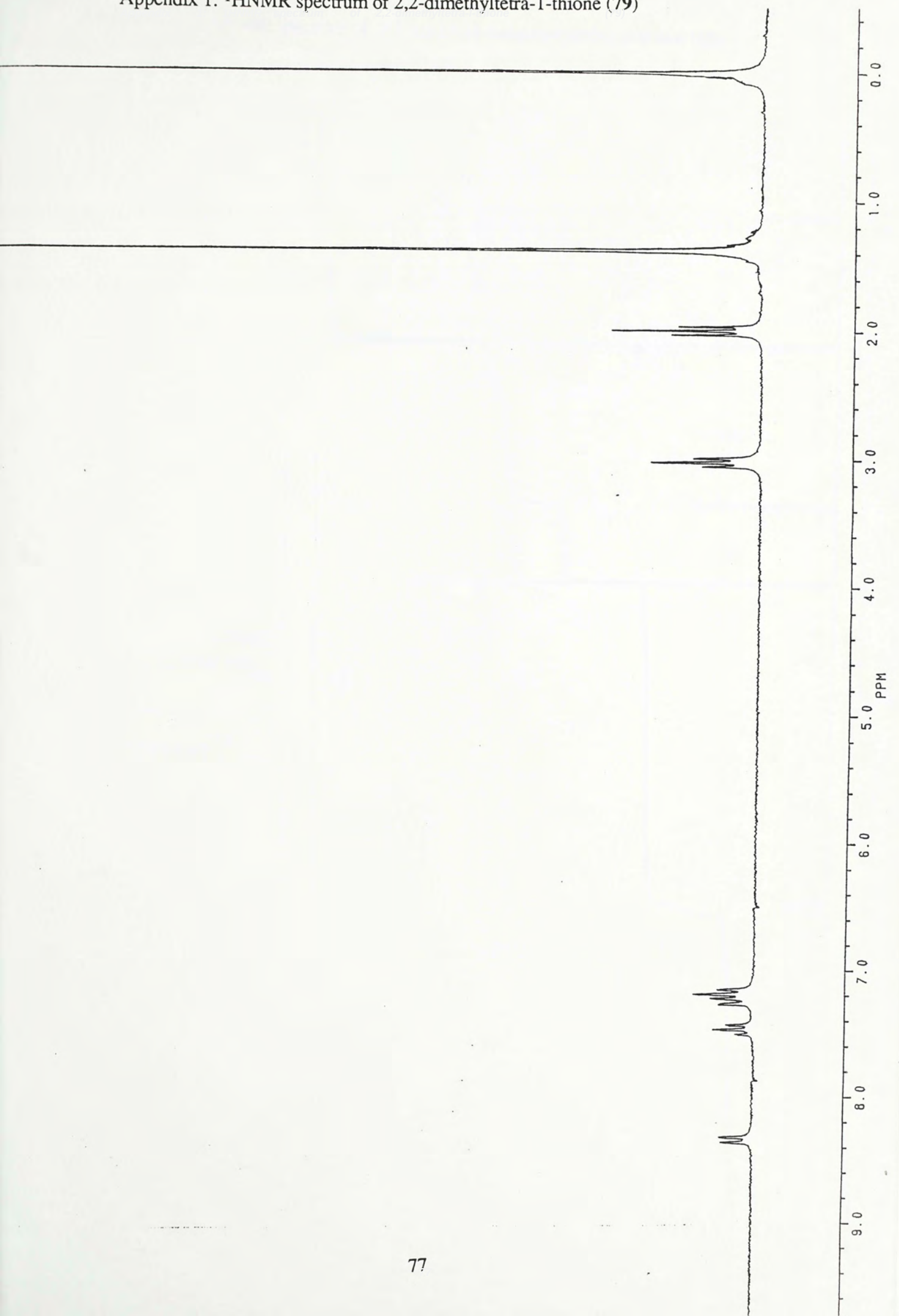
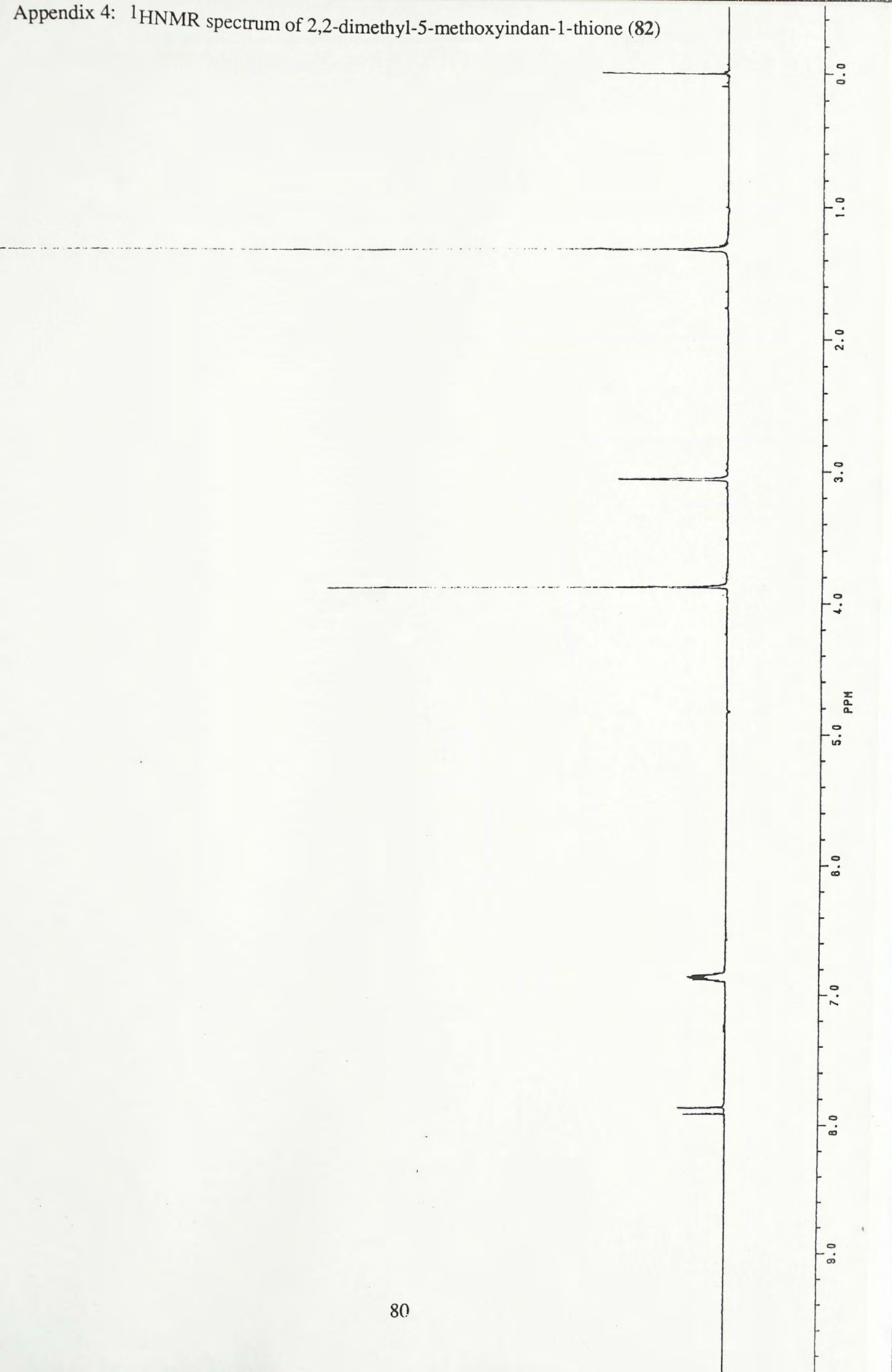
Appendix 1: ^{1}HNMR spectrum of 2,2-dimethyltetra-1-thione (**79**)



Appendix 2: ^{1}HNMR spectrum of 2,2-dimethyl-6-methoxyindan-1-thione (**80**)

Appendix 3: ^{1}HNMR spectrum of 2,2,6-trimethylindan-1-thione (**81**)

Appendix 4: ^{1}HNMR spectrum of 2,2-dimethyl-5-methoxyindan-1-thione (**82**)



Appendix 5: ^{1}HNMR spectrum of 2,2,5-trimethylindan-1-thione (83)